Organic Syntheses via Transition Metal Complexes. 117.[1] 3-Aza-1-metalla-1,3,5-hexatrienes (M = Cr, W): Generation and π-Cyclization to Pyrroles

Rudolf Aumann,* Dominik Vogt, and Roland Fröhlich†

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

Received December 4, 2001

3-Aza-1-metallahexa-1,3,5-trienes **3a**−**f** were obtained in good yields by condensation of the (NH_2-amino)carbene complexes $(CO)_5M{=}C(Ph)NH_2$ (**1a**,**b**; M = Cr, W) with α,β-unsaturated acid amides **2** in the presence of phosphoryl chloride and triethylamine. Compounds **3** undergo a thermally induced π-cyclization to pyrroles **4**.

Introduction

The term "azametallahexatriene" has been established as a convenient nomenclature for a group of metal carbene complexes in which a nitrogen atom is incorporated into the ligand backbone of a metallahexatriene[2] (Chart 1). Since 1-metalla-1,3,5-hexatrienes of chromium and tungsten were found to readily undergo a π-cyclization to cyclopentadiene complexes, 5-aza-1-metalla-1,3,5-hexatrienes were considered as the most likely candidates for the formation of N-heterocyclic compounds in an analogous reactions. It could indeed be shown that 5-aza-1-metalla-1,3,5-hexatrienes gave 2*H*-pyrrole complexes by a "typical" π-cyclization, but in addition these compounds were found to also afford dihydropyridones by an "atypical" π-cyclization involving a chain extension by insertion of carbon monoxide. Generation of pyrroles and dihydropyridones by π-cyclization of 5-aza-1-metalla-1,3,5-trienes was achieved by two different approaches, in which the 5-aza-1-metalla-1,3,5-trienes were generated either by insertion of an alkyne into the M=C bond of an iminocarbene complex ("alkyne route to pyrroles")[3,4] or by addition of a *NH*-imino group to a (1-alkynyl)carbene complex ("imine route to pyrroles").[5,6] Following these findings, we decided to perform some systematic studies on the chemistry of azametallahexatrienes. Since 5-aza-1-metalla-1,3,5-hexatrienes and cross-conjugated azametallahexatrienes[7] have been the only compounds studied so far (Chart 1), we decided to next extend our investigation to 3-aza-1-metalla-1,3,5-hexatrienes of chromium and tungsten.

Results and Discussion

3-Aza-1-metallahexa-1,3,5-trienes. We now report on the preparation of 3-aza-1-metallahexa-1,3,5-trienes, which gained our interest as potential precursors to pyrroles. Our strategy was based on the condensation of (NH_2-amino)carbene complexes $(CO)_5M{=}C(NH_2)Ph$ (**1a**,**b**; M = Cr, W) with α,β-unsaturated acid amides **2**. Related condensation reactions of (NH_2-amino)carbene complexes **1a**,**b** with the acid amides R^1CONR_2 (R = alkyl, aryl) to give 4-amino-3-aza-1-metalla-1,2-butadienes $(CO)_5M{=}C(Ph)N{=}C(NR_2)R^1$,[8,9] with aldehydes RCHO (R = aryl) to give 3-aza-1-metalla-1,2-butadienes $(CO)_5M{=}C(Ph)N{=}CHR$, and with acid chlorides RCOCl (R = aryl) to yield 4-acyloxy-3-aza-1-metalla-1,2-butadienes $(CO)_5M{=}C(Ph)N{=}C(OCOR)R$ have been previously described.[8,10]

Condensation of the aminocarbene complex **1** with the α,β-unsaturated acid amide **2** in the presence of phosphoryl chloride and triethylamine indeed afforded 3-aza-1-metallahexa-1,3,5-trienes **3** in good yields (Scheme 1). It is obvious that this reaction was initiated by the transformation of the α,β-unsaturated acid amide **2** into the iminium chloride **5**, which is an electrophile strong enough to interact with the aminocarbene complex **1**.

* To whom correspondence should be addressed.
† X-ray structure analysis.

(1) For part 116 of this series see: Aumann, R.; Vogt, D.; Fu, X.; Fröhlich, R.; Schwab, P. *Organometallics*, in press.

(2) For a recent review on metallahexatrienes see: Aumann, R. *Eur. J. Org. Chem.* **2000**, 17−31.

(3) Dragisich, V.; Murray, C. K.; Warner, B. P.; Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 1251.

(4) (a) Aumann, R.; Heinen, H. *J. Organomet. Chem.* **1990**, *389*, C1. (b) Aumann, R.; Heinen, H. *J. Organomet. Chem.* **1990**, *391*, C7. (c) Aumann, R., Heinen, H.; Krüger, C.; Betz, P. *Chem. Ber.* **1990**, *123*, 599−604. (d) Aumann, R., Heinen, H.; Krüger, C.; Betz, P. *Chem. Ber.* **1990**, *123*, 605−610. (e) Aumann, R.; Heinen, H.; Dartmann, M.; Krebs, B. *Chem. Ber.* **1991**, *124*, 2587−2593.

(5) Funke, F.; Duetsch, M.; Stein, F.; Noltemeyer, M.; de Meijere, A. *Chem. Ber.* **1994**, *127*, 911.

(6) Aumann, R.; Fröhlich, R.; Zippel, F. *Organometallics* **1997**, *16*, 2571.

(7) (a) Aumann, R.; Jasper, B.; Fröhlich, R.; Zippel, F. *Organometallics* **1995**, *14*, 3167. (b) Aumann, R.; Yu, Z.; Fröhlich, R.; Zippel, F. *Eur. J. Inorg. Chem.* **1998**, 1623.

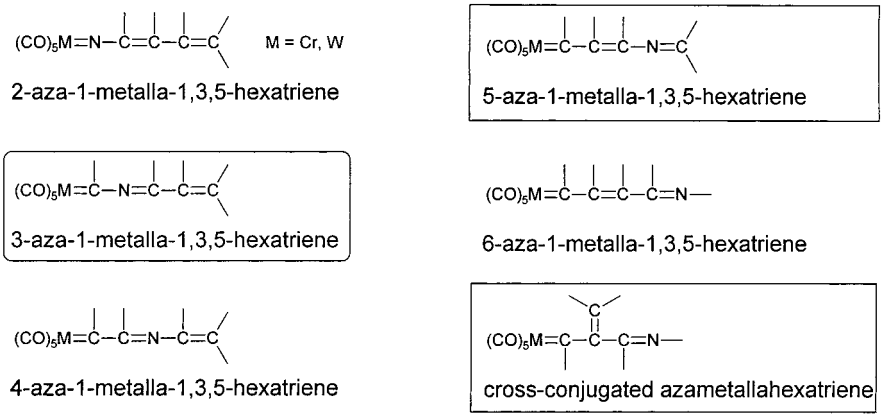
(8) Aumann, R.; Althaus, S.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 357.

(9) For the generation of 4-amino-3-aza-1-metalla-1,3-butadiene from aminocarbene complexes and inamines see: (a) Dötz, H. H. *Chem. Ber.* **1980**, *113*, 3597. (b) Dötz, K. H. *J. Organomet. Chem.* **1976**, *118*, C13.

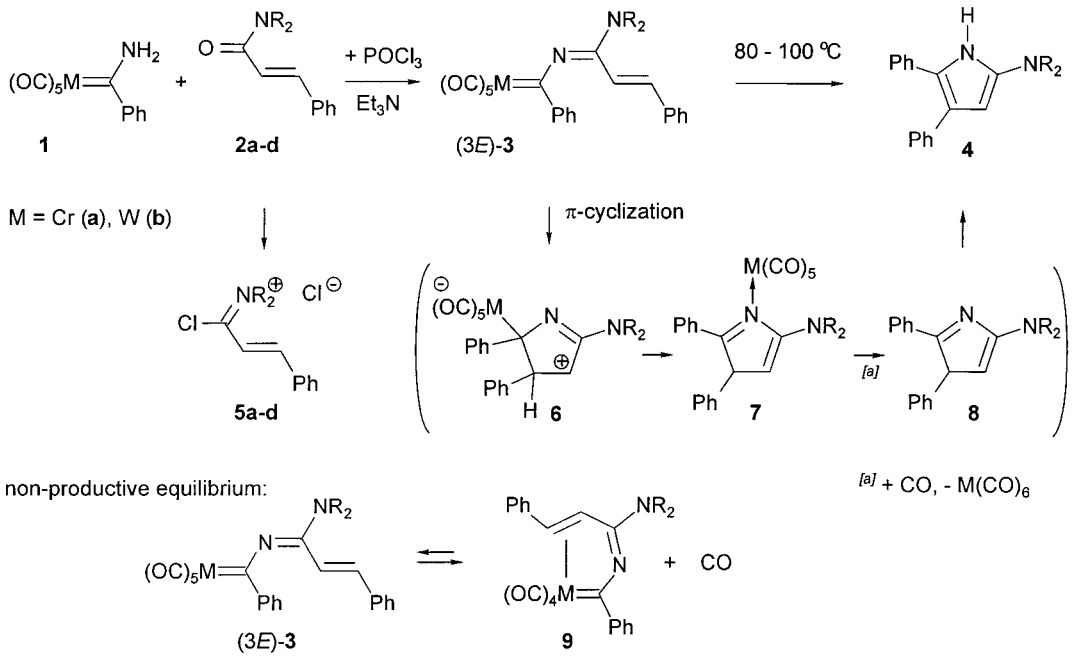
(10) For earlier work on similar structures see: (a) Fischer, H. *J. Organomet. Chem.* **1980**, *197*, 303. (b) Fischer, H.; Schubert, U.; Märkl, R. *Chem Ber.* **1981**, *114*, 3412. (c) Fischer, H.; Märkl, R. *Chem. Ber.* **1985**, *118*, 3683. (d) Fischer, H.; Seitz, F.; Müller, G. *J. Organomet. Chem.* **1987**, *320*, 185. (e) Fischer, H.; Schubert, U. *Angew. Chem.* **1981**, *93*, 482; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 461. (f) Fischer, H.; Zeuner, S.; Ackermann, K.; Schubert, U. *J. Organomet. Chem.* **1984**, *263*, 201. (g) Seitz, F.; Fischer, H.; Riede, J. *J. Organomet. Chem.* **1985**, *287*, 87. (h) Fischer, H.; Zeuner, S. *J. Organomet. Chem.* **1987**, *327*, 63. (i) Yang, D. C.; Dragisich, V.; Wulff, W. D.; Huffman, C. *J. Am. Chem. Soc.* **1988**, *110*, 307. (j) Fischer, E. O.; Hollfelder, H.; Kreissl, F. R.; Uedelhoven, W. *J. Organomet. Chem.* **1976**, *113*, C31. (k) Knauss, L.; Fischer, E. O. *Chem. Ber.* **1970**, *103*, 3744.

10.1021/om011032d CCC: $22.00
Publication on Web 04/04/2002

Chart 1. Basic Structures of Azametallahexatrienes (M = Cr, W)



Scheme 1. 3-Aza-1-metalla-1,3,5-hexatrienes 3: Generation from Aminocarbene Complexes 1 and Transformation into Pyrroles 4

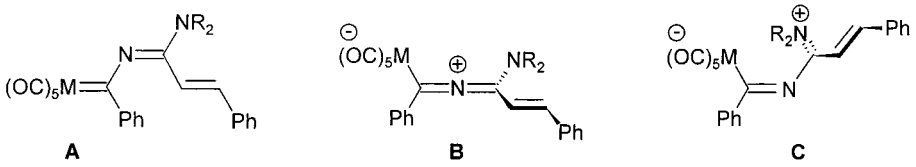


1	2	3,4	M	NR_2	3[a]	4[a]	9
a	**a**	**a**	Cr	NMe_2	71	82	-
a	**b**	**b**	Cr	pyrrolidino	84	80	-
a	**c**	**c**	Cr	morphcolino	79	-	-
b	**a**	**d**	W	NMe_2	82	79	-
b	**b**	**e**	W	pyrrolidino	42	78	15[b]
b	**d**	**f**	W	$N(Me)CH_2Ph$	57	78	-[c]

[a] Isolated yields in percent. [b] Isolated in small amount from the equilibrium mixture. [c] Not isolated, but analyzed in a mixture with compound **3f**.

Pyrroles by Thermolysis of 3-Aza-1-metalla-1,3,5-hexatrienes. Thermolysis of 3-aza-1-metallahexatrienes **3** requires 80−100 °C and leads to production of pyrroles **4**. This process is assumed to involve the π-cyclization of compound **3** into the zwitterionic intermediate **6**, from which the 2*H*-pyrrole complex **7** is obtained by a 1,2-transfer of the $M(CO)_5$ unit (Scheme 1). (5,6-η^2)-3-Aza-1-metallahexa-1,3,5-trienes **9** have been detected in the reaction mixture in varying amounts, depending on the reaction conditions. These compounds are generated in a nonproductive equilibrium by chelation of compounds (3*E*)-**3** involving the loss of a carbonyl ligand. Thermally induced ligand disengagement from 2*H*-pyrrole complexes **7** affords the thermolabile 2*H*-pyrroles **8** and finally the stable 1*H*-pyrroles **4**. While 2*H*-pyrrole complexes **7** could not be isolated under these reaction conditions, it was possible to obtain and fully characterize 2*H*-pyrrole complexes from π-cyclization of 5-aza-1-metallahexa-1,3,5-trienes under mild conditions.[4c,6] The relatively high reaction temperature of 80−100 °C required for the π-cyclization of 3-aza-1-metallahexa-1,3,5-trienes **3** is attributed not only to the low

Chart 2. Basic Structures of Compounds 3 with Different Geometries: Iminocarbene Structure A, 2-Azaallenyl Structure B, and Iminium Carbonylmetalate Structure C



electrophilicity of aminocarbene complexes but also to the lack of stabilization of the positive charge in the zwitterionic intermediate **6**.

Structure of 3-Aza-1-metalla-1,3,5-hexatrienes. The 3-aza-1-metalla-1,3,5-hexatrienes **3** were characterized by ^{1}H and ^{13}C NMR spectra, including ^1J(C,H) and $^{2,3}J$(C,H) correlation experiments performed with compounds **3a**,**e**. The temperature dependence of the NMR spectra was extensively studied with compounds **3d**−**f**. Compound **3d** was characterized also by a crystal structure analysis. The ^{13}C NMR signals of the carbene carbon atom are observed in a narrow range characteristic of the specific metal unit [e.g. **3a** (30 °C) δ(Cr=C) 253.9, **3d** (30 °C) δ(W=C) 236.7]. Since this range is appreciably shifted upfield compared to aminocarbene complexes of the corresponding metal unit [e.g. $(CO)_5$W=*C*(OEt)CH=C(NMe$_2$)Ph at δ 271.5, $(CO)_5$W=*C*(NH$_2$)-Ph at δ 264.2], it was thought that compounds **3** would adopt the 2-azaallenyl structure **B** or the iminium carbonylmetalate structure **C** instead of the iminocarbene structure **A** (Chart 2). Experimental proof for this assumption was provided both by NMR studies and by a crystal structure analysis of compound **3a**. Since structures **B** and **C** were expected to be chiral, methylene protons attached to the terminal nitrogen atom, as in compound **3f** [NR$_2$ = N(Me)CH$_2$Ph], served as a probe for the structure elucidation by NMR experiments.[11]

Since the ^{1}H NMR spectrum of compound **3f** exhibited a singlet for the NCH$_3$ group (δ 3.19) and an AB system for the NC*H*$_2$Ph unit (δ 4.98 and 4.63, ^2J = 16.5 Hz; 10 °C, 360 MHz, Figure 1), an iminocarbene structure **A** of this compound was excluded.

The line shape of the proton signals of the CH$_2$N unit of compound **3f** was strongly temperature dependent (Figure 1). A "frozen spectrum" obtained at −55 °C showed two AB systems at δ 5.45 and 4.25 (^2J = ca. −15 Hz) and δ 4.86 and 4.70 (^2J = ca. −17 Hz), which collapsed to one AB system above 10 °C and finally gave a single signal above 75 °C. The assignment of signals is based on spin saturation transfer experiments, in order to minimize the uncertainty resulting from the temperature drift of the signals. On the basis of the coalescence temperature and the difference of chemical shifts, it was possible to distinguish between two different dynamic processes, for which $\Delta G^{\ddagger}$ values of ca. 50 and 70 kJ/mol were estimated.

The crystal structure analysis of compound **3a** (Figure 2) reveals a strongly bent CNC unit, C1−N2−C3 = 137.9°, in which the plane defined by the atoms C1, N2, and C3 is tilted by 84.3° against the plane defined the atoms N6, C3, and C4. The distance C1−N2 = 1.282(3) Å is shorter than N2−C3 = 1.322(3) Å and also shorter than C3−N6 = 1.335(3) Å, thus indicating a strong charge delocalization, as is represented by the iminium carbonylmetalate structure **C** (Chart 2), which according to the dynamic NMR spectra of compound **3f** (Figure 1)

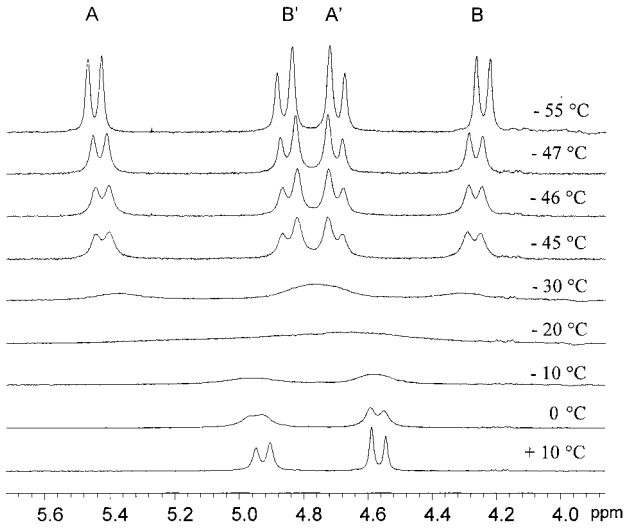


Figure 1. ^{1}H NMR signals of the NCH$_2$ group of compound **3f** in [D$_8$]toluene in the temperature range from −55 to +10 °C.

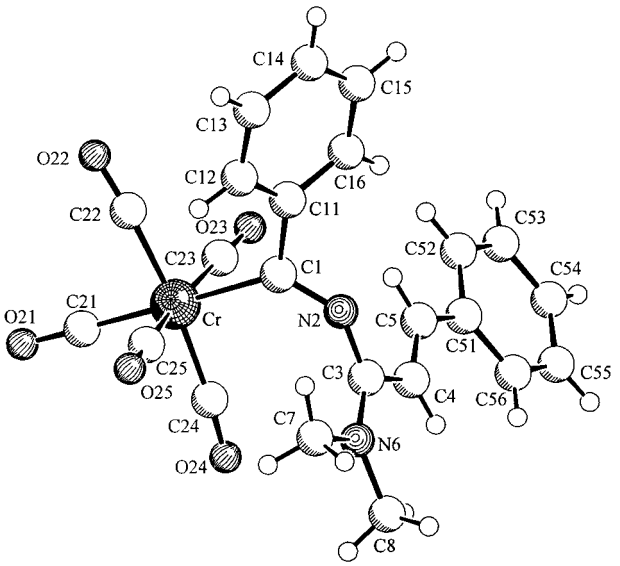


Figure 2. Molecular structure of the 4-amino-1-metalla-1,3,5-hexatriene **3a**. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): Cr−C1 = 2.114(2), C1−N2 = 1.282(3), N2−C3 = 1.322(3), C3−C4 = 1.462(3), C4−C5 = 1.313 (3), C5−C51 = 1.461(3), C3−N6 = 1.335(3), C1−C11 = 1.506(3); N2−C1−Cr = 127.5(2), C1−N2−C3 = 137.9(2), N2−C3−C4 = 118.7(2), N6−C3−C4 = 120.8(2); Cr−C1−N2−C3 = −6.2(4), C1−N2−C3−N6 = −84.3(4), C1−N2−C3−C4 = 102.9(3), N2−C3−C4−C5 = −10.2(4), N6−C3−C4−C5 = 177.0(2), C3−C4−C5−C51 = 178.3(2), C4−C5−C51−C52 = 173.3 (3).

(11) Dötz, K. H.; Muhlemeier, U.; Schubert, U.; Orama, O. *J. Organomet. Chem.* **1983**, *247*, 187.

as well as the crystal structure analysis of compound **3a** is considered the most adequate structural description of the compound **3**.

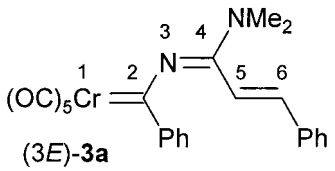
Conclusion. A new entry to the formation of pyrroles from the readily available (NH_2-amino)carbene complexes $(CO)_5M{=}C(Ph)NH_2$ (**1a**,**b**; M = Cr, W) was found. It involves generation of 3-aza-1-metallahexa-1,3,5-trienes **3** by condensation of compounds **1** with α,β-unsaturated acid amides **2** and subsequent π-cyclization of these compounds to pyrroles **4**. The reaction is highly regioselective. The reaction may in principle be extended to the synthesis of pyrroles other than those containing amino functionalities.

Experimental Section

Instrumentation. NMR: Bruker AM 360, Bruker AMX 400, and Varian U 600. All new compounds were routinely analyzed by ^{1}H, ^{13}C, DEPT, (^{1}H,^{1}H)COSY, (^{1}H,^{13}C)GHSQC, and (^{1}H,^{13}C)GHMBC experiments on a Bruker AMX 400 instrument. IR: FT-IR Bio-Rad Digilab Division FTS-45. MS: Finnigan MAT8200. Elemental analyses: Heraeus CHN-O Rapid. Column chromatography: Merck silica gel 60F. Flash chromatography was performed under an argon atmosphere. TLC: Merck silica gel $60F_{254}$. R_f values refer to TLC tests.

4-(Dimethylamino)-2,6-diphenyl-3-aza-1-pentacarbonylchroma-1,3,5-hexatriene (3a) and 2-(Dimethylamino)-4,5-diphenyl-*1H*-pyrrole (4a). To *N*,*N*-dimethyl-3-phenylacrylamide (**2a**; 263 mg, 1.50 mmol) and 2 mL of dry dichloromethane in a 5 mL screw-top vessel was added phosphoryl chloride (229 mg, 1.50 mmol) with stirring at 0 °C. To the pale yellow precipitate that was formed within ca. 30 min was added a mixture of pentacarbonyl(α-NH_2-aminobenzylidene)-chromium (**1a**; 149 mg, 0.50 mmol) and triethylamine (505 mg, 5.00 mmol) in 1 mL of dry dichloromethane. Stirring was continued at 20 °C for 24 h. Flash chromatography of the mixture on silica gel (column 20 × 2 cm) with *n*-pentane afforded colorless hexacarbonylchromium, which was discarded. Elution with *n*-pentane/dichloromethane (3:1) yielded a red fraction containing the 3-aza-1-chroma-1,3,5-hexatriene **3a** (161 mg, 71%, R_f = 0.4 on silica gel with *n*-pentane/dichloromethane (2:1), red crystals from dichloromethane/diethyl ether at −20 °C, dec pt 74 °C). Thermolysis of compound **3a** (150 mg, 0.33 mmol) in 2 mL of benzene at 80 °C for 14 h gave hexacarbonylchromium and 2-(dimethylamino)-4,5-diphenyl-*1H*-pyrrole (**4a**), which was isolated by chromatography on silica gel (71 mg, 82%, pale yellow oil).

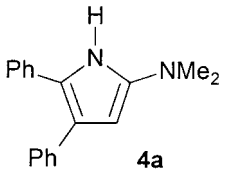
3a.



(3*E*)-**3a**

^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.57 (2 H, m, Ph), 7.46−7.33 (9 H, m, 2-Ph, 6-Ph, and 6-H), 6.82 (1 H, d, ^3J = 15 Hz, 5-H), 3.24 (6 H, s broad, 2 NCH_3). ^{13}C NMR ($CDCl_3$): δ 253.9 (Cr=C), 224.2 and 218.7 (1:4, *trans*- and *cis*-CO $Cr(CO)_5$), 152.8 (C_q broad, C4), 152.3 (C_q, *i*-C 2-Ph), 145.4 (CH, C6), 134.4 (C_q, *i*-C 6-Ph), 130.7, 129.0, 128.3, 128.1, 127.8 and 123.3 (1:2:2:2:1:2, CH each, 2-Ph and 6-Ph), 114.4 (CH, C5), 39.2 (2 NCH_3). IR (*n*-hexane; cm^{-1} (%)): 2047.2 (30), 1928.1 (100) (ν(C≡O)). MS (70 eV; *m*/*e* (%)): 454 (0) [M^+], 398 (10) [M^+ − 2 CO], 342 (1) [M^+ − 4 CO], 314 (52) [M^+ − 5 CO], 262 (100) [M^+ − $Cr(CO)_5$]. Anal. Calcd for $C_{23}H_{18}N_2CrO_5$ (454.4): C, 60.79; H, 3.99; N, 6.16. Found: C, 60.82; H, 3.84; N, 6.21. Crystal structure analysis of compound **3a** (code AUM_711): formula $C_{23}H_{18}N_2O_5Cr$, M_r = 454.39, red crystal, 0.60 × 0.50 × 0.40 mm, *a* = 9.515(1) Å, *b* = 14.935(2) Å, *c* = 16.036(1) Å, β = 102.34(1)°, *V* = 2226.2(4) Å^3, ρ_{calcd} = 1.356 g cm^{-3}, *F*(000) = 936 e, μ = 5.49 cm^{-1}, empirical absorption correction via φ scan data (0.948 ≤ *C* ≤ 0.999), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, *T* = 293 K, ω/2θ scans, 4790 reflections collected (−*h*, -*k*, ±*l*), (sin θ)/λ = 0.62 Å^{-1}, 4516 independent and 2988 observed reflections ($I \geq 2\sigma(I)$), 282 refined parameters, R1 = 0.039, wR2 = 0.108, maximum residual electron density 0.29 (−0.21) e Å^{-3}, hydrogens calculated and refined as riding atoms.

4a.



4a

^{1}H NMR (C_6D_6, 303 K, 360 MHz): δ 7.78 (1 H, NH), 7.58, 7.26, 7.20−6.90 (CH each, 2:2:6 H, 4-Ph and 5-Ph), 5.65 (1 H, d, ^4J = 3 Hz, 3-H), 2.38 (6 H, s, 2 NCH_3). ^{13}C NMR (C_6D_6): δ 145.1 (C_q, C2), 138.1 and 134.5 (C_q each, *i*-C each of 4-Ph and 5-H), 128.9, 128.7, 128.6, and 126.7 (CH each, 2:2:2:2, *o*-CH and *m*-CH each of 2 Ph), 125.9 and 125.8 (CH each, *p*-C each Ph), 122.4 and 122.3 (C_q each, C4 and C5), 93.9 (CH, C3), 42.5 (2 NCH_3). IR (diffuse reflection; cm^{-1}): 3329.8 (ν(N−H)). MS (70 eV; *m*/*e* (%)): 262 (80) [M^+], 247 (100), 206 (15), 131 (9), 104 (10), 103 (5).

2,6-Diphenyl-4-pyrrolidino-3-aza-1-pentacarbonylchroma-1,3,5-hexatriene (3b) and 4,5-Diphenyl-2-pyrrolidino-1*H*-pyrrole (4b). 3-Phenyl-1-pyrrolidinoprop-2-en-1-one (**2b**; 201 mg, 1.00 mmol) was reacted with phosphoryl chloride (145 mg, 0.95 mmol), pentacarbonyl(α-NH_2-aminobenzylidene)-chromium (**1a**; 149 mg, 0.50 mmol), and triethylamine (505 mg, 5.00 mmol) as described above to give compound **3b** (202 mg, 84%, R_f = 0.4 on silica gel with *n*-pentane/dichloromethane (2:1), red crystals from dichloromethane/diethyl ether at −20 °C, dec pt 68 °C). Thermolysis of 4-pyrrolidino-3-aza-1-chroma-1,3,5-hexatriene (**3b**) in 2 mL of dry toluene at 100 °C as described above afforded the pale yellow compound **4b** in ca. 80% yield.

3b. ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.57 (2 H, m, Ph), 7.47 (1 H, d, ^3J = 16 Hz, 6-H), 7.44−7.22 (8 H, m, 2-Ph and 6-Ph), 6.74 (1 H, d, ^3J = 16 Hz, 5-H), 3.69 (4 H, m broad, 2 NCH_2), 2.12 (4 H, m broad, 2 NCH_2CH_2). ^{13}C NMR ($CDCl_3$): δ 253.3 (Cr=C), 224.2 and 219.0 (1:4, *trans*- and *cis*-CO $Cr(CO)_5$), 153.9 and 153.3 (C_q broad each, C4 and *i*-C 2-Ph), 145.9 (CH, C6), 134.3 (C_q, *i*-C 6-Ph), 130.8, 129.1, 128.5, 128.0, 127.4 and 123.0 (1:2:2:2:1:2, CH each, 2-Ph and 6-Ph), 115.0 (CH, C5), 48.7 (2 NCH_2), 25.1 (2 NCH_2CH_2). IR (*n*-hexane; cm^{-1} (%)): 2048.1 (25), 1929.0 (100) (ν(C≡O)). MS (70 eV; *m*/*e* (%)): 480 (0) [M^+], 424 (10) [M^+ − 2 CO], 340 (60) [M^+ − 5 CO], 288 (100) [M^+ − $Cr(CO)_5$]. Anal. Calcd for $C_{25}H_{20}N_2CrO_5$ (480.4): C, 62.50; H, 4.20; N, 5.83. Found: C, 62.31; H, 4.40; N, 5.70.

4b. ^{1}H NMR (C_6D_6, 303 K, 360 MHz): δ 7.80 (1 H, NH), 7.60, 7.31, and 7.28−6.85 (CH each, 2:2:6 H, 2 Ph), 5.48 (1 H, d, ^4J = 3 Hz, 3-H), 2.77 (4 H, m broad, 2 NCH_2), 1.49 (4 H, m broad, 2 NCH_2CH_2). ^{13}C NMR (C_6D_6): δ 144.2 (C_q, C2), 138.5 and 134.7 (C_q each, *i*-C each 4-Ph and 5-Ph), 129.0, 128.8, 128.6, 126.9, 125.9, and 125.4 (CH each, 2:2:2:2:2, 2 Ph), 123.0 and 120.8 (C_q each, C4 and C5), 90.9 (CH, C3), 49.3 (2 NCH_2), 25.1 (2 NCH_2CH_2). IR (diffuse reflection; cm^{-1}): 3329.7 (ν(N−H)). MS (70 eV; *m*/*e* (%)): 288 (70) [M^+], 232 (100), 217 (80).

4-Morpholino-2,6-diphenyl-3-aza-1-pentacarbonylchroma-1,3,5-hexatriene (3c). 1-Morpholino-3-phenylprop-2-en-1-one (**2c**; 217 mg, 1.00 mmol) was reacted with phosphoryl chloride (145 mg, 0.95 mmol), pentacarbonyl(α-NH_2-aminobenzylidene)chromium (**1a**; 149 mg, 0.50 mmol), and triethylamine (505 mg, 5.00 mmol) as described above to give

compound **3c** (196 mg, 79%, $R_f = 0.2$ on silica gel in *n*-pentane/dichloromethane (2:1), red crystals, dec pt 82 °C).

3c. ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.52 (2 H, m, Ph), 7.43−7.29 (8 H, m, 2-Ph and 6-Ph), 7.29 (1 H, d, $^3J = 15$ Hz, 6-H), 6.77 (1 H, d, $^3J = 15$ Hz, 5-H), 3.87 (4 H, m, 2 OCH_2), 3.58 (4 H, m broad, 2 NCH_2). ^{13}C NMR ($CDCl_3$): δ 252.9 (Cr=C), 224.0 and 218.4 (1:4, *trans*- and *cis*-CO $Cr(CO)_5$), 150.3 (C_q, *i*-C 2-Ph), 145.4 (C_q broad, C4), 144.6 (CH, C6), 134.3 (C_q, *i*-C 6-Ph); 130.6, 129.1, 128.6, 128.3, 128.2, and 123.9 (1:2:1:2:2:2, CH each, 2-Ph and 6-Ph), 113.9 (CH, C5), 66.0 (2 OCH_2), 46.8 (2 NCH_2). IR (*n*-hexane; cm^{-1} (%)): 2047.3 (30), 1929.2 (100) (ν(C≡O)). MS (70 eV; *m/e* (%)): 496 (1) [M^+], 440 (2) [$M^+ - 2$ CO], 384 (1) [$M^+ - 4$ CO], 356 (30) [$M^+ - 5$ CO], 304 (100) [$M^+ - Cr(CO)_5$]. Anal. Calcd for $C_{25}H_{20}N_2CrO_6$ (496.4): C, 60.49; H, 4.06; N, 5.64. Found: C, 60.53; H, 4.07; N, 5.56.

4-(Dimethylamino)-2,6-diphenyl-3-aza-1-pentacarbonyltungsta-1,3,5-hexatriene (3d) and 2-(Dimethylamino)-4,5-diphenyl-*1H*-pyrrole (4a). *N,N*-Dimethyl-3-phenylacrylamide (**2a**; 175 mg, 1.00 mmol), phosphoryl chloride (145 mg, 0.95 mmol), pentacarbonyl(α-NH_2-aminobenzylidene)tungsten (**1b**; 215 mg, 0.50 mmol), and triethylamine (505 mg, 5.00 mmol) were reacted as described above to give compound **3d** (240 mg, 82%, $R_f = 0.4$ on silica gel in *n*-pentane/dichloromethane (2:1), red crystals from dichloromethane/diethyl ether at −20 °C, dec pt 73 °C). Thermolysis of the 3-aza-1-pentacarbonyltungsta-1,3,5-hexatriene **3d** (293 mg, 0.50 mmol) in 2 mL of dry toluene at 100 °C for 14 h afforded 2-(dimethylamino)-4,5-diphenyl-*1H*-pyrrole (**4a**; 104 mg, 79%, pale yellow oil), which was isolated by chromatography on silica gel.

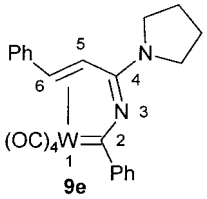
3d. ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.59 (2 H, m, Ph), 7.50−7.38 (9 H, m; 2-Ph, 6-Ph and 6-H), 6.83 (1 H, d, $^3J = 15$ Hz, 5-H), 3.32 (6 H, s, 2 NCH_3). ^{1}H NMR (C_6D_6, 303 K, 360 MHz): δ 7.69 (2 H, m, Ph), 7.41 (1 H, d, $^3J = 15$ Hz, 6-H), 7.26−7.00 (8 H, m, 2-Ph and 6-Ph), 6.30 (1 H, d, $^3J = 15$ Hz, 5-H), 2.36 (6 H, s, 2 NCH_3). ^{13}C NMR (C_6D_6): δ 236.7 (W=C), 203.8 and 200.8 (1:4, *trans*- and *cis*-CO $W(CO)_5$), 156.7 (C_q broad, C4), 153.6 (C_q, *i*-C 2-Ph), 146.6 (CH, C6), 134.7 (C_q, *i*-C 6-Ph), 130.8, 129.2, 129.0, 128.6, 128.3, and 126.0 (1:2:1:2:2:2, CH each, 2-Ph and 6-Ph), 114.3 (CH, C5), 38.4 (2 NCH_3). IR (diffuse reflection; cm^{-1}): 2052.4, 1960.7, 1900.4 (ν(C≡O)). IR (*n*-hexane; cm^{-1} (%)): 2056.2 (15), 1924.9 (100) (ν(C≡O)). MS (70 eV, ^{184}W; *m/e* (%)): 586 (1) [M^+], 530 (1) [$M^+ - 2$ CO], 502 (1) [$M^+ - 3$ CO], 474 (1) [$M^+ - 4$ CO], 446 (2) [$M^+ - 5$ CO], 262 (40) [$M^+ - W(CO)_5$], 99 (100). Anal. Calcd for $C_{23}H_{18}N_2O_5W$ (586.3): C, 47.12; H, 3.09; N, 4.78. Found: C, 47.12; H, 3.87; N, 4.81.

4a. See above for spectroscopic data.

2,6-Diphenyl-4-pyrrolidino-3-aza-1-pentacarbonyltungsta-1,3,5-hexatriene (3e), $\eta^{5,6}$-2,6-Diphenyl-4-pyrrolidino-3-aza-1-tetracarbonyltungsta-1,3,5-hexatriene (9e) and 4,5-Diphenyl-2-pyrrolidinopyrrole (4b). 3-Phenyl-1-pyrrolidinoprop-2-en-1-one (**2b**; 201 mg, 1.00 mmol), phosphoryl chloride (145 mg, 0.95 mmol), pentacarbonyl(α-NH_2-aminobenzylidene)tungsten (**1b**; 215 mg, 0.50 mmol), and triethylamine (505 mg, 5.00 mmol) were reacted as described above to give compound **3e** (129 mg, 42%, $R_f = 0.4$ on silica gel in *n*-pentane/dichloromethane (2:1), red crystals from dichloromethane/diethyl ether at −20 °C, dec pt 76 °C). A suspension of pentacarbonyl-4-pyrrolidino-3-aza-1-pentacarbonyltungsta-1,3,5-hexatriene (**3e**; 490 mg, 0.80 mmol) in 2 mL of C_6D_6 was heated to 80 °C. It was shown by TLC tests that the red compound **3e** ($R_f = 0.4$ in *n*-pentane/dichloromethane (2:1)) disappears gradually, while the dark brown chelate compound **9e** ($R_f = 0.2$ in *n*-pentane/dichloromethane (2:1)) was formed. According to an ^{1}H NMR spectrum after 6 h at 80 °C a 3:2:1 mixture of pyrrolidino-3-aza-1-tungsta-1,3,5-hexatriene (**3e**), 2-pyrrolidino-*1H*-pyrrole (**4b**), and the chelate complex **9e** was obtained. A ^{1}H NMR spectrum after 18 h at 80 °C indicated a product ratio of 1:3:1 for these compounds. The mixture was separated on silica gel (column 20 × 2 cm) with *n*-pentane to afford colorless hexacarbonyltungsten. Elution with *n*-pentane/dichloromethane (3:1) yielded a red fraction with compound **3e** (38 mg, 8%, $R_f = 0.4$ in *n*-pentane/dichloromethane (2:1) and a dark brown fraction containing compound **9e** (72 mg, 15%, $R_f = 0.2$ in *n*-pentane/dichloromethane (2:1)). Subsequent elution with *n*-pentane/diethyl ether (1:1) afforded a pale yellow fraction with 4,5-diphenyl-2-pyrrolidinopyrrole (**4b**; 92 mg, 40%). Thermolysis of compound **3e** (240 mg, 0.50 mmol) at 100 °C for 16 h in toluene as described above gave 4,5-diphenyl-2-pyrrolidino-*1H*-pyrrole (**4b**; 112 mg, 78%).

3e. ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.59 (2 H, m, Ph), 7.53 (1 H, d, $^3J = 15$ Hz, 6-H), 7.47−7.33 (8 H, m, 2-Ph and 6-Ph), 6.71 (1 H, d, $^3J = 15$ Hz, 5-H), 3.70 (4 H, m broad, 2 NCH_2), 2.14 (4 H, s broad, 2 NCH_2CH_2). ^{13}C NMR ($CDCl_3$): δ 236.5 (W=C), 204.0 and 201.0 (1:4, *trans*- and *cis*-CO $W(CO)_5$), 158.5 (C_q broad, C4), 154.4 (C_q, *i*-C 2-Ph), 147.5 (CH, C6), 134.3 (C_q, *i*-C 6-Ph), 131.1, 129.1, 128.6, 128.2, 127.9, and 124.9 (1:2:2:1:2:2, CH each, 2-Ph and 6-Ph), 114.7 (CH, C5), 45.4 (2 NCH_2), 25.0 (2 NCH_2CH_2). IR (diffuse reflection; cm^{-1} (%)): 2052.4 (35), 1960.7 (40) 1900.4 (100) (ν(C≡O)). MS (70 eV, ^{184}W; *m/e* (%)): 612 (2) [M^+], 584 (1) [$M^+ -$ CO], 556 (1) [$M^+ - 2$ CO], 528 (6) [$M^+ - 3$ CO], 500 (5) [$M^+ - 4$ CO], 472 (7) [$M^+ - 5$ CO], 288 (100) [$M^+ - W(CO)_5$].

9e.



9e

^{1}H NMR ([D_8]toluene): δ 8.37 (2 H, "d", *o*-CH Ph), 7.30−7.05 (8 H, m, Ph), 4.83 and 4.29 (1 H each, AB system, $^3J = 10$ Hz, CH=CHPh), 3.42, 2.98, 2.65, and 2.51 (1:1:1:1, m each, diastereotopic NCH_2), 1.05 (4 H, m, NCH_2CH_2). ^{13}C NMR (C_6D_6): δ 276.3 (W=C), 222.6, 212.1, 210.8, and 209.7 (C_q each, 1:1:1:1, CO each $W(CO)_4$), 178.1 (C_q, C4), 149.6 and 142.0 (C_q each, *i*-C each, Ph), 132.1, 130.2, 129.0, 128.3, 127.4, and 125.8 (CH each, 1:2:2:2:1:2, 2-Ph and 6-Ph), 73.9 and 59.5 (CH each, *C*H=*C*HPh), 50.3 and 49.1 (2 NCH_2), 25.0 and 24.4 (2 NCH_2CH_2). IR (*n*-hexane; cm^{-1} (%)): 2056.2 (40), 1922.5 (100) (ν(C≡O)). MS (70 eV, ^{184}W; *m/e* (%)): 584 (5) [M^+], 556 (5) [$M^+ -$ CO], 528 (15) [$M^+ - 2$ CO], 500 (10) [$M^+ - 3$ CO], 472 (20) [$M^+ - 4$ CO], 288 (100) [$M^+ - W(CO)_4$], 184 (15), 149 (30).

4b. See above for spectroscopic data.

4-(Benzylmethylamino)-2,6-diphenyl-3-aza-1-pentacarbonyltungsta-1,3,5-hexatriene (3f), $\eta^{5,6}$-4-(Benzylmethylamino)-2,6-diphenyl-3-aza-1-tetracarbonyltungsta-1,3,5-hexatriene (9f), and 4-(Benzylmethylamino)-2,6-diphenyl-*1H*-pyrrole (4f). (Benzylmethylamino)-3-phenylacrylamide (**2d**; 502 mg, 2.00 mmol), phosphoryl chloride (290 mg, 1.90 mmol), pentacarbonyl(α-NH_2-aminobenzylidene)tungsten (**1b**; 429 mg, 1.00 mmol), and triethylamine (1010 mg, 10.00 mmol) were reacted as described above to give compound **3f** (337 mg, 57%, $R_f = 0.4$ on silica gel in *n*-pentane/dichloromethane (2:1), red crystals from dichloromethane/diethyl ether at −20 °C, dec pt 68 °C). The NMR spectrum of a solution resulting from thermolysis of compound **3f** (169 mg, 0.25 mmol) in [D_8]toluene in an NMR tube at 80 °C for 15 min shows signals of the pyrrole **4f** and the chelate compound **9f** in a molar ratio of ca. 1:6. Compound **9f** exhibits two sets of signals in a ratio of ca. 3:1, resulting from isomers due to hindered rotation of the C−N bond. The spectra could be assigned only partially, due to overlapping signals. Thermolysis of compound **3f** (169 mg, 0.25 mmol) in [D_8]toluene at 80 °C for 12 h afforded the pyrrole **4f** (256 mg, 78%).

3f. ^{1}H NMR ($CDCl_3$, 303 K, 360 MHz): δ 7.52 and 7.48 (2 H each, m each, 2 Ph), 7.44−7.35 (8 H, m, 2-Ph, 6-Ph and 6-H),

7.34−7.28 (4 H, m, Ph), 6.83 (1 H, d, ^3J = 15 Hz, 5-H), 4.92 and 4.57 (1 H each, d each broad, ^2J = 16 Hz, diastereotopic NCH_2), 3.16 (3 H, s, NCH_3). ^{13}C NMR ($CDCl_3$): δ 237.1 (W═C), 204.0 and 199.9 (1:4, *trans*- and *cis*-CO $W(CO)_5$), 153.7 (C_q broad, C4), 152.2 (C_q, *i*-C 2-Ph), 146.4 (CH, C6), 134.5 and 134.1 (each C_q, *i*-C 6-Ph and *i*-C NCH_2Ph), 130.8, 129.2, 129.1, 129.0, 128.9, 128.4, 128.3, 128.0, and 127.3 (1:2:2:1:1:2:2:2:2, CH each; 2-Ph, 6-Ph and NCH_2Ph), 113.8 (CH, C5), 54.9 (NCH_2), 37.1 (NCH_3). IR (diffuse reflection; cm^{-1}): 2052.4, 1960.7, 1900.4 (ν(C≡O)). IR (*n*-hexane; cm^{-1} (%)): 2056.2 (15), 1924.9 (100) (ν(C≡O)). MS (70 eV, ^{184}W; *m*/*e* (%)): 662 (1) [M^+], 606 (1) [M^+ − 2 CO], 578 (1) [M^+ − 3 CO], 550 (1) [M^+ − 4 CO], 522 (2) [M^+ − 5 CO], 338 (40) [M^+ − $W(CO)_5$], 99 (100).

3f (isomer ratio ca. 2:1; signals of minor isomer in braces). ^{1}H NMR ($CDCl_3$, 213 K, 360 MHz): δ 7.70−7.25 (32 H, m broad, 6 Ph and 2 C*H*═CHPh), 5.44 and 4.25 {4.87 and 4.70} (1 H each, d broad each, ^2J = 15 Hz each, diastereotopic NCH_2 each), 3.21 {3.19} (3 H, s, NCH_3). ^{13}C NMR ($CDCl_3$, 213 K, 90 MHz): δ 240.6 {236.2} (C_q, W═C), 204.5 and 199.8 (C_q each, 1:4, *trans*- and *cis*-CO $W(CO)_5$), 156.6 {160.3} (C_q, C4), 152.1 {153.1} (C_q, *i*-C Ph), 148.3 {147.0} (CH, CH═*C*HPh), 133.9, 133.5, and 133.4 (C_q each, 2:1:1, *i*-C each of 6-Ph and CH_2Ph), 131.2, 129.1, 128.6, 126.4, 125.8 {131.0, 129.0, 128.8, 128.6, 128.4, 126.4} (CH each, 2 Ph), 113.2 {112.8} (CH, *C*H═CHPh), 54.7 {53.9} (NCH_2), 37.9 {36.5} (NCH_3).

9f. ^{1}H NMR ([D_8]toluene, 300 K) (partial assignment, signals of minor isomer in brackets, if observed): 8.25 (2 H, "d", *o*-CH each of 2-Ph and 6-Ph), 6.92 (4 H, m, Ph), 4.85 and 4.42 {4.80 and 4.49} (1 H each, d each, ^3J = 11 Hz, C*H*═C*H*Ph), 4.78, 4.40, and 4.02 (m each, diastereotopic NCH_2 each), 2.91 and 2.48 (1:3 H, s each, NCH_3 each). ^{13}C NMR ([D_8]toluene, 300 K): δ 272.0 (W═C, broad), 222.3, 211.7, 210.7, 209.4 (C_q each, 1:1:1:1, $W(CO)_4$), 183.6 {183.0} (C_q each, 1:3, C4), 150.3 and 142.0 {150.2 and 142.1} (C_q each, 3:3:1:1, *i*-C each of 2-Ph and 6-Ph), 134.9 {133.9} (C_q each, 3:1, *i*-C NCH_2*Ph* each), 132.3−130.3 (CH each, Ph), 74.5 {74.4} (CH each, 3:1, CH═CHPh), 56.2 {56.2} (NCH_2 each, 3:1), 39.1 and 37.3 (NCH_3 each).

4f. ^{1}H NMR ([D_8]toluene, 300 K): δ 7.50 (2 H, "d", Ph), 7.30−7.00 (14 H, m, Ph and NH), 5.61 (1 H, d, ^4J = 3 Hz, 3-H), 3.86 (2 H, s, NCH_2), 2.46 (3 H, s, NCH_3). ^{13}C NMR ([D_8]toluene, 300 K; partial assignment only): δ 144.5 (C_q, C2), 138.8, 138.1, and 134.4 (C_q each, *i*-C Ph each), 122.3 and 121.8 (C_q each, C4 and C5), 94.3 (CH, C3), 59.5 (NCH_2), 39.5 (NCH_3). MS (70 eV; *m*/*e* (%)): 338 (90) [M^+], 233 (100).

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables giving details of the X-ray crystal structure analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

OM011032D