Novel (Imino-η^6-arene)chromium Complexes and Their Diastereoselective Intramolecular Hetero-Diels–Alder Reactions

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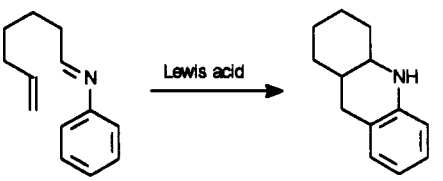
Novel (imino-η^6-arene)chromium complexes **3** with nonactivated olefins tethered to the 2-azadiene system were prepared and further used in a new diastereoselective intramolecular Lewis-acid-catalyzed hetero-Diels–Alder reaction to give (η^6-octahydroacridine)chromium complexes **4**. The trans selectivity of the cyclization reaction is mainly controlled by the $Cr(CO)_3$ fragment and to a minor extent by the catalyst, solvent, and substituents. Complexes **4** also could be obtained by a one-pot reaction starting from aldehyde **1**, (*o*-toluidine)$Cr(CO)_3$ (**2**), and Lewis acid. The stereochemistry of **4a** was established by single-crystal X-ray structure analysis. Compound **4a** crystallized in the monoclinic space group $P2_1/c$ with a = 9.518(1) Å, b = 12.456(1) Å, c = 16.457(1) Å, β = 90.79(1)°, V = 1950.8 Å^3, Z = 4, R = 0.038 R_w = 0.045, and T = 293 K for 343 parameters and 4426 reflections.

Introduction

The use of chromium arene complexes in organic synthesis has increased in recent years. This is due to the fact that the strongly electron withdrawing $Cr(CO)_3$ fragment activates the arene toward nucleophilic addition reactions and proton abstractions. It also stabilizes both benzylic anions and cations by increasing the kinetic acidity of benzylic protons and enhancing the solvolysis rate, respectively. Another major effect of the chromium tricarbonyl group is the steric shielding of one face of the aromatic ring by the bulky metal fragment, thus directing the attack of an incoming reagent to the exo face. Therefore, chromium arene complexes have been very successfully used in different types of diasteroselective syntheses.[1] Whereas diastereoselective, nucleophilic additions to carbonyl groups attached to the arene tricarbonyl moiety have been studied extensively,[2] the corresponding chemistry with imines remains rather unexplored.[3] The only reported examples have been addition of organolithiums,[4] Grignard reagents,[5] and borohydrides[4] to imines and transaminations.[6] Continuing the studies on our recently found intramolecular Lewis-acid-catalyzed hetero-Diels–Alder reaction of *N*-arylimines (eq 1),[7] we were



(1)

interested in whether this reaction type could be applied to chromium arene complexes. If this would be the case, the $Cr(CO)_3$ fragment would further activate the imine by its electron-withdrawing ability and therefore function as an internal Lewis acid. The steric bulkiness of the chromium tricarbonyl moiety should also increase the cis/trans selectivity of the newly formed ring junction. In this article we report on syntheses of previously unknown tricarbonylchromium imino complexes derived from (*o*-toluidine)$Cr(CO)_3$ and unsaturated aliphatic aldehydes and their highly diastereoselective Lewis-acid-catalyzed cyclization to (octahydroacridine)$Cr(CO)_3$ complexes.

Results and Discussion

In order to avoid aldol condensation of the aliphatic aldehydes under the usual acidic conditions of imine formation (catalyst TsOH, refluxing benzene),[4] we used a milder method to prepare the imino complexes. Thus,

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(2) (a) Solladié-Cavallo, A.; Bencheqroun, M. *J. Organomet. Chem.* **1991**, *406*, C15–C19. (b) Uemura, M.; Oda, H.; Minami, T.; Hayashi, Y. *Tetrahedron Lett.* **1991**, *32*, 4565–4568. (c) Uemura, M.; Miyake, R.; Shiro, M.; Hayashi, Y. *Tetrahedron Lett.* **1991**, *32*, 4569–4572. (d) Bromley, L. A.; Davies, S. G.; Goodfellow, C. L. *Tetrahedron: Asymmetry* **1991**, *2*, 139–156. (e) Solladié-Cavallo, A.; Lapitajs, G.; Buchert, P.; Klein, A.; Colonna, S.; Manfredi, A. *J. Organomet. Chem.* **1987**, *330*, 357–363. (f) Solladié-Cavallo, A.; Suffert, J. *Tetrahedron Lett.* **1984**, *25*, 1897–1900. (g) Uemura, M.; Minami, T.; Shiro, M.; Hayashi, Y. *J. Org. Chem.* **1992**, *57*, 5590–5596. (h) Alexakis, A.; Mangeney, P.; Marek, I.; Rose-Munck, F.; Rose, E.; Semra, A.; Robert, F. *J. Am. Chem. Soc.* **1992**, *114*, 8288–8290. (i) Uemura, M.; Oda, H.; Minami, T.; Shiro, M.; Hayashi, Y. *Organometallics* **1992**, *11*, 3705–3712.

(3) For reactions of chromium tricarbonyl phenylmethanimines see: (a) Kündig, E. P.; Bernardinelli, G.; Liu, R.; Ripa, A. *J. Am. Chem. Soc.* **1991**, *113*, 9676–9677. (b) Kündig, E. P.; Amurio, D.; Liu, R.; Ripa, A. *Synlett* **1991**, 657–658. (c) Blagg, J.; Davies, S. G.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc. Perkin Trans. 1* **1987**, 1805–1811.

(4) Bloem, P.; David, D. M.; Kane-Maguire, L. A. P.; Pyne, S. G.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1991**, *407*, C19–C22.

(5) Solladié-Cavallo, A.; Tsamo, E. *J. Organomet. Chem.* **1979**, *172*, 165–169.

(6) Solladié-Cavallo, A.; Farkhanj, D. *Tetrahedron Lett.* **1986**, *27*, 1331–1334.

(7) Laschat, S.; Lauterwein, J. *J. Org. Chem.* **1993**, *58*, 2856–2861.

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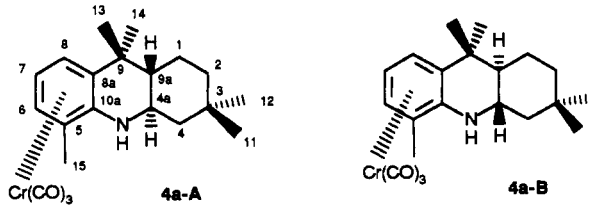
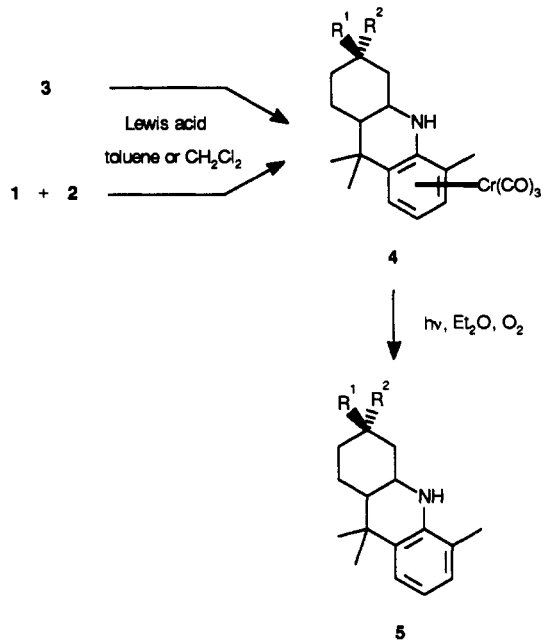
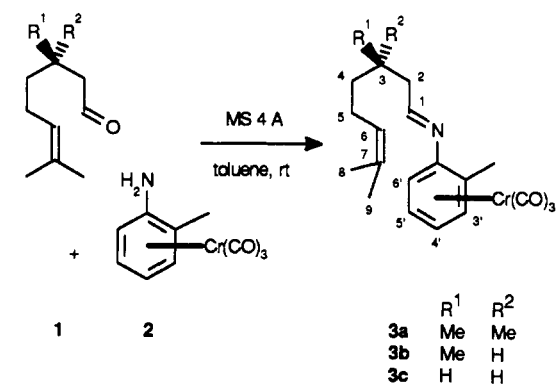


Figure 1. Two possible diastereomers of the chromium complex **4a**.

Scheme I



the aldehydes 1 (R^1, R^2 = H, Me) were reacted with racemic (*o*-toluidine)chromium tricarbonyl (**2**)[8] in toluene solution at room temperature in the presence of 4-Å molecular sieves to give the imino complexes **3** in almost quantitative yield (eq 2). After removal of the molecular sieves by filtration



(2)

	1	2	R^1	R^2
3a			Me	Me
3b			Me	H
3c			H	H

the solution of **3** was used for the cyclization reaction without further isolation and purification.

Reaction of the imino complex **3a** (R^1 = R^2 = Me) with catalytic amounts of $SnCl_4$ (0.1 equiv) in toluene at −78 °C for 80 h gave the (1,2,3,4,4a,9,9a,10-octahydroacridine)-chromium tricarbonyl complex **4a** in very high yield (98%) with exclusive formation of the trans product (Scheme I; Table I, entry 1). The cis/trans ratios were determined by oxidative decomplexation, i.e. exposure of ethereal

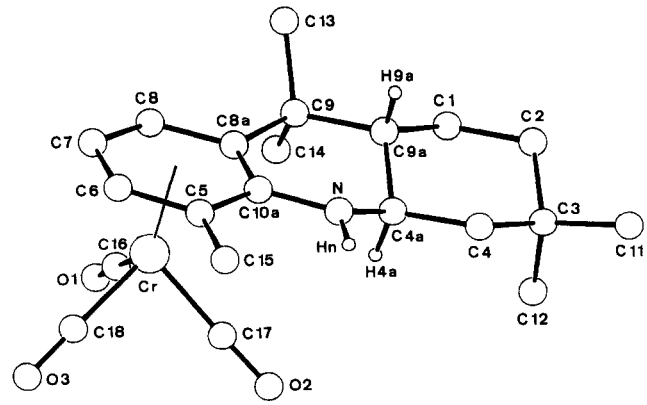


Figure 2. X-ray crystal structure of **4a**.

solutions of the crude cyclization products **4** to sunlight in the presence of air,[2i] followed by capillary GC analysis. In each case the trans isomers **4** were the major products irrespective of the solvent, Lewis or Brønsted acid, or type of aldehyde used. However, the yields dropped markedly when CH_2Cl_2 was used as a solvent instead of toluene (Table I, entries 1 and 6), and the chromium-free cyclization products **5** were observed as major byproducts. A decrease in steric bulkiness of the substituents at C-3 of the imino complex **3** resulted in a slight decrease of the amount of trans product **4** (Table I, entries 1, 10, and 12) from 0/100 for **4a** to 3.8/96.2 for **4c**. However, this effect of the C-3 substituents on the cis/trans selectivity is much smaller than in the above-mentioned chromium-free cyclization of *N*-arylimines (eq 1).[7] In that case the cis/trans ratio could be completely changed from 1/99 cis/trans for the *gem*-dimethyl-substituted imine to 64/36 for the unsubstituted imine. Therefore, the sterically demanding $Cr(CO)_3$ fragment seems to play a major role in determining the stereochemistry, i.e. the cis/trans ratio of the ring fusion, whereas substituents on the carbon skeleton of the cyclization precursor **3** have only a minor influence. Attempts to perform the cyclization as a one-pot reaction were again extremely dependent on the solvent. Thus, addition of the Lewis acid to a precooled solution of (toluidine)$Cr(CO)_3$ (**2**) in toluene followed by slow addition of the aldehyde **1** (method B) resulted in a high yield of **4** with excellent trans selectivity (entry 5). In contrast, when the same reaction was run in CH_2Cl_2, only 33% of **4a** was isolated (entry 7). Even the addition of molecular sieves during the tandem imine condensation/cyclization reaction (method C) to remove the water, which might decrease the yield due to hydrolysis, did not improve the yields significantly (entry 8). However, the isolation of suitable amounts of the chromium-free products shows that the cyclization itself is not suppressed by CH_2Cl_2, but the decomplexation reaction is favored especially in the presence of protic acid catalysts.

Independently from GLC analysis of the decomplexation products **5**,[9] the trans ring fusion of **4a** was clearly established by ^1H NMR spectroscopy. The ddd resonance at 3.12 ppm ($J_{4a,4ax}$ = 11 Hz, $J_{4a,9a}$ = 11 Hz, $J_{4a,4eq}$ = 4 Hz) was assigned to H-4a. The other products **4b,c** showed similar couplings. In order to differentiate between the two possible diastereomeric chromium complexes **4aA** and **4aB** (Figure 1), which could not be distinguished by NMR, the molecular structure of **4a** was determined by an X-ray

(8) Compound **2** was used in its racemic form, which is commercially available. For an optical resolution procedure see: Rosca, S.; Nenitzescu, C. D. *Rev. Roum. Chim.* **1970**, *15*, 259–263; *Chem. Abstr.* **1970**, *73*, 3370p.

(9) Spectroscopic data for the decomplexation products **5** are given in ref 7.

Table I. Cyclization of Imino-arene Complexes 3

entry no.	R^1	R^2	solvent	temp (°C)	Lewis acid (amt, equiv)	time (h)	yield (%)	method[a]	cis/trans
1	Me	Me	toluene	−78	$SnCl_4$ (0.1)	80	98	A	0/100
2	Me	Me	toluene	−78 to room temp	TFA (1.0)	8	92	A	0.4/99.6
3	Me	Me	toluene	−78	HBF_4 (1.0)[b]	14	78	A	0.4/99.6
4	Me	Me	toluene	room temp[c]	$TsOH{\cdot}H_2O$ (1.0)	40	31	A	3.0/97.0
5	Me	Me	toluene	−78	$SnCl_4$ (0.1)	20	98	B	0.2/99.8
6	Me	Me	CH_2Cl_2	−78	$SnCl_4$ (0.1)	23	30[d]	A	0.6/99.4
7	Me	Me	CH_2Cl_2	−78	$SnCl_4$ (0.1)	18	33[d]	B	0/100
8	Me	Me	CH_2Cl_2	−78	$SnCl_4$ (0.1)	50	41[d]	C	0/100
9	Me	Me	CH_2Cl_2	room temp[c]	$ZnCl_2{\cdot}OEt_2$ (0.1)	24	27[d]	A	0.7/99.3
10	Me	H	toluene	−78	$SnCl_4$ (0.1)	26	50	A	1.3/97.3/1.4/0.0[e]
11	Me	H	CH_2Cl_2	−78	$SnCl_4$ (0.1)	12	34	B	23.9/72.6/2.9/0.7[e]
12	H	H	toluene	−78	$SnCl_4$ (0.1)	27	41	A	3.8/96.2

[a] Method A: a solution of **3** in toluene was used. Method B: one-pot reaction, the reactants were added in the order (1) amine, (2) Lewis acid, (3) aldehyde. Method C: same conditions as in method B, but finally 4-Å molecular sieves was added. [b] A solution (54%, v/v) of HBF_4 in Et_2O was used. [c] No conversion at −78 °C for 14 h. [d] Varying amounts of the chromium-free cyclization product were isolated: 9% (entry 6), 39% (entry 7), 27% (entry 8), 36% (entry 9). [e] The configuration of the two minor diastereomers was not established.

Table II. Atomic Coordinates for 4a

atom	x	y	z
Cr	0.0597(1)	0.7958(1)	0.6302(1)
O(1)	0.1988(2)	1.0091(1)	0.6466(1)
O(2)	0.0687(2)	0.7807(1)	0.8106(1)
O(3)	0.3488(2)	0.7013(2)	0.6314(1)
C(1)	−0.4411(3)	0.9686(2)	0.7535(2)
C(2)	−0.5390(3)	0.9236(2)	0.8157(2)
C(3)	−0.4687(3)	0.8425(2)	0.8733(2)
C(4)	−0.3993(3)	0.7565(2)	0.8211(2)
C(5)	−0.0815(2)	0.6522(2)	0.6088(1)
C(6)	−0.0050(3)	0.6751(2)	0.5387(1)
C(7)	−0.0098(3)	0.7760(3)	0.5021(1)
C(8)	−0.0911(3)	0.8548(2)	0.5370(1)
C(9)	−0.2718(2)	0.9252(2)	0.6361(1)
C(11)	−0.5834(4)	0.7907(3)	0.9246(3)
C(12)	−0.3609(4)	0.8967(4)	0.9289(3)
C(13)	−0.3640(4)	0.9628(3)	0.5640(2)
C(14)	−0.1857(3)	1.0218(2)	0.6671(2)
C(15)	−0.0767(3)	0.5411(2)	0.6450(2)
C(16)	0.1433(2)	0.9270(2)	0.6386(1)
C(17)	0.0663(2)	0.7870(2)	0.7406(1)
C(18)	0.2369(3)	0.7375(2)	0.6293(1)
C(4a)	−0.2994(2)	0.8005(2)	0.7585(1)
C(8a)	−0.1737(2)	0.8373(2)	0.6067(1)
C(9a)	−0.3715(2)	0.8816(2)	0.7025(1)
C(10a)	−0.1693(2)	0.7328(2)	0.6418(1)
N	−0.2485(2)	0.7119(1)	0.7090(1)
H(4a)	−0.218(2)	0.832(2)	0.786(1)
H(9a)	−0.439(2)	0.841(2)	0.674(1)
Hn	−0.231(2)	0.658(2)	0.734(1)

Table III. Selected Bond Lengths (Å) and Angles (deg) for 4a

Cr–C(16)	1.823(2)	Cr–C(17)	1.822(2)
Cr–C(18)	1.837(3)	O(1)–C(16)	1.158(3)
O(2)–C(17)	1.154(3)	O(3)–C(18)	1.157(3)
C(5)–C(6)	1.403(3)	C(5)–C(10a)	1.419(3)
C(6)–C(7)	1.394(4)	C(7)–C(8)	1.381(4)
C(8)–C(8a)	1.418(3)	C(9)–C(8a)	1.523(3)
C(9)–C(9a)	1.555(3)	C(4a)–C(9a)	1.525(3)
C(4a)–N	1.459(3)	C(4a)–H(4a)	0.98(2)
C(8a)–C(10a)	1.425(3)	C(9a)–H(9a)	0.93(2)
C(10a)–N	1.372(3)	N–Hn	0.80(2)
C(18)–Cr–C(17)	88.0(1)	C(18)–Cr–C(16)	87.4(1)
C(17)–Cr–C(16)	88.2(1)	C(10a)–C(5)–C(6)	119.1(2)
C(7)–C(6)–C(5)	121.7(2)	C(8)–C(7)–C(6)	118.5(2)
C(8a)–C(8)–C(7)	123.2(2)	C(9a)–C(9)–C(8a)	110.8(2)
O(1)–C(16)–Cr	177.5(2)	O(2)–C(17)–Cr	179.0(2)
O(3)–C(18)–Cr	177.7(2)	H(4a)–C(4a)–N	107(1)
H(4a)–C(4a)–C(9a)	112(1)	N–C(4a)–C(9a)	108.3(2)
C(10a)–C(8a)–C(9)	122.9(2)	C(10a)–C(8a)–C(8)	117.1(2)
C(9)–C(8a)–C(8)	119.7(2)	H(9a)–C(9a)–C(4a)	104(1)
H(9a)–C(9a)–C(9)	105(1)	C(4a)–C(9a)–C(9)	112.5(2)
N–C(10a)–C(8a)	119.1(2)	N–C(10a)–C(5)	120.5(2)
C(8a)–C(10a)–C(5)	120.4(2)	Hn–N–C(10a)	117(2)
Hn–N–C(4a)	115(2)	C(10a)–N–C(4a)	119.8(2)

diffraction analysis. Figure 2 clearly shows the syn relationship between H-4a and the $Cr(CO)_3$ moiety in **4a** (atomic coordinates, selected bond lengths and angles, and details of the structure determination are shown in Tables II–IV). The syn-eclipsed orientation of the $Cr(CO)_3$ tripod is in complete agreement with X-ray crystallographic determinations of other chromium arene complexes containing electron-donating substituents.[10,11] This is rationalized by the polarization of the charge distribution in the ring by the electron-donating group, which results in an increased donor ability of the ortho and para carbon atoms. To maintain the preferred octahedral geometry at chromium, the carbonyl ligands have to eclipse the ipso and meta positions.

With regard to the stereochemical results of the cyclization, a concerted hetero-Diels–Alder type mechanism seems much likelier than in the previously reported chromium-free case.[7] As shown in Scheme II, in the possible transition state **6** the tethered dienophile can attack only the top face of the 2-azadiene moiety because the bottom face is completely shielded by the bulky chromium tricarbonyl fragment. The boat geometry of the transition state results in the formation of the trans fused ring system, where the syn position (relative to chromium) is occupied by H-4a and the anti position by H-9a. However, this model does not explain the influence of the C-3 substituent on the cis/trans ratio, although the $Cr(CO)_3$ ligand obviously has the most important effect on the stereochemistry. The corresponding transition state **8**, which leads to the cis fused ring system, should be strongly disfavored as compared to **6** because of the severe steric interactions between the $Cr(CO)_3$ fragment and the dienophile moiety approaching the 2-azadiene from the bottom face.

Conclusion

The new (imino-arene)chromium complexes **3** described above are synthetically useful for the highly trans-selective preparation of (octahydroacridine)chromium complexes **4**. Especially, the organic decomplexation products **5** seem

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(11) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 3, pp 953–1077.

Table IV. Details of the Data Collection and Structure Solution of 4a[a]

mol formula	$C_{21}H_{27}CrNO_3$
mol wt	393.5
cryst color	yellow
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	9.518(1)
b, Å	12.456(1)
c, Å	16.457(1)
β, deg	90.79(1)
V, Å^3	1950.8
Z	4
D_{calcd}, g cm^{-3}	1.34
μ, cm^{-1}	5.90
Mo Kα radiation: λ, Å	0.710 69
$F(000)$, e	832
diffractometer	Enraf-Nonius CAD4
scan mode	ω–2θ
$[(\sin\theta)/\lambda]_{max}$, Å^{-1}	0.65
T, °C	20
no. of measd rflns ($\pm h,+k,+l$)	4796
no. of indep rflns	4426
no. of obsd rflns ($I > 2\sigma(I)$)	3412
no. of refined params	343
R	0.038
R_w ($w = 1/\sigma^2(F_o)$)	0.045
resid electron dens, e Å^{-3}	0.27
structure soln	heavy-atom method

[a] The H atom positions were found and included in the final refinement stages.

to be interesting targets for further pharmacological studies.[12-14] The easy access to imino complexes **3** and the convenient one-pot cyclization reaction allow for the diastereoselective preparation of a wide variety of substituted octahydroacridines just by choosing suited aldehydes **1** and arene complexes **2**.

Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. Analytical TLC was performed on precoated Merck Si 254 F plates (0.25-mm thickness) and visualized with a solution of phosphomolybdic acid in EtOH (5%, v/v). Flash chromatography was carried out with Merck silica gel 60 (230–400 mesh). NMR spectra were recorded on a Bruker AC 200 P (200 MHz, ^{1}H; 50 MHz, ^{13}C) and a Bruker AM 360 (360 MHz, ^{1}H; 90.5 MHz, ^{13}C) spectrometer. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet 5DXC FT-IR spectrometer. Optical rotations were measured in 1-dm cells (1 mL capacity) on a Perkin-Elmer Model 241 polarimeter at ambient temperature. Mass spectra were obtained with a Finnigan Model MAT 312 spectrometer (ionization potential 70 eV). For GC analysis an HP5 fused silica capillary column (i.d. 0.32 mm, length 25 m) was used. 7-Methyl-6-octenal and 3,3,7-trimethyl-6-octenal were prepared according to literature procedures;[15] (*R*)-(+)-citronellal and (*o*-toluidine)chromium tricarbonyl were commercially available.

General Procedure for the Preparation of Imine Complexes 3. To a solution of (*o*-toluidine)Cr(CO)$_3$ (**2**; 243 mg, 1.00 mmol) in toluene (20 mL) was added aldehyde **1** (1.00 mmol) and powdered 4-Å molecular sieves (1.00 g), and the remaining mixture was stirred for 12 h at room temperature. After filtration through Celite via a fritted funnel, the solution could be used for the cyclizations without further isolation and purification. Only complex **3a** was isolated and completely characterized.

Tricarbonyl[*N*-(3,3,7-trimethyl-6-octenylidene)-*o*-toluidine]chromium (3a). Evaporation of the solvent at room temperature under high vacuum yielded 354 mg (90%) of a yellow oil (imine/aldehyde = 84.5/15.5, determined by ^{1}H NMR):[16] ^{1}H NMR (200 MHz, C_6D_6) δ 7.81 (t, J = 6 Hz, 1 H, H-1), 5.17 (m, 1 H, H-6), 4.78–4.67 (m, 1 H, H-6′), 4.58–4.31 (m, 2 H, H-4′, H-5′), 4.09–4.01 (m, 1 H, H-3′), 2.17–1.10 (m, 6 H, H-2, H-5, H-4), 1.79 [s, 3 H, (C-2′)CH_3], 1.67 (s, 3 H, H-8), 1.57 (s, 3 H, H-9), 0.92 [s, 6 H, (C-3)(CH_3)$_2$]; ^{13}C NMR (50 MHz, C_6D_6) δ 235.3 (CO), 171.3 (C-1), 131.1 (C-7), 128.5 (C-1′), 125.0 (C-6), 103.0 (C-2′), 93.0, 92.3, 89.1, 88.6 (C-3′, C-4′, C-5′, C-6′), 54.5 (C-2), 47.6 (C-5), 42.8 (C-4), 27.4 [(C-3)(CH_3)$_2$], 27.3 (C-8), 25.8 (C-9), 23.1 (C-3), 17.0 [(C-2′)CH_3]; IR (film) 2962 (m), 2930 (m), 2872 (m), 1961 (vs, ν_{CO}), 1876 (vs, ν_{CO}), 1719 (m, $\nu_{CO,aldehyde}$), 1661 (w), 630 (m) cm^{-1}; MS (EI) *m/e* 393 (M, 19), 309 (40), 242 (24), 225 (54), 185 (73), 174 (65), 161 (42), 118 (91), 91 (49), 69 (63), 52 (100); HRMS calcd for $C_{21}H_{27}NO_3Cr$ 393.1396, found 393.1391.

General Procedure for the Cyclization of Imine Complexes 3. For catalysts, temperatures, and reaction times, see Table I. To a solution of the imine complex **3** (1.00 mmol) in toluene or CH_2Cl_2 (28 mL) was added the Lewis acid over 30 min, and the resulting mixture was stirred until TLC showed no more conversion. Then was added 2 N NaOH (100 mL), and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). After the combined organic layers were washed with saturated NaCl (200 mL), dried over $MgSO_4$, and evaporated, the crude products were purified by flash chromatography on SiO_2 (5/1 hexanes/Et_2O).

Tricarbonyl(*trans*-3,3,5,9,9-pentamethyl-1,2,3,4,4a,9,-9a,10-octahydroacridine)chromium (4a). Flash chromatography yielded 360 mg (92%) of yellow crystals: mp 168 °C dec; ^{1}H NMR (200 MHz, C_6D_6) δ 5.18 (d, J = 7 Hz, 1 H, H-6), 4.97 (d, J = 6 Hz, 1 H, H-8), 4.20 (dd, J = 7 Hz, J = 6 Hz, 1 H, H-7), 3.17 (s, broad, 1 H, NH), 3.12 (ddd, J = 11 Hz, J = 11 Hz, J = 4 Hz, 1 H, H-4a), 1.56 (s, 3 H, H-15), 1.54–0.76 (m, 7 H, H-1, H-2, H-4, H-9a), 1.21 (s, 3 H, H-13), 0.87 (s, 3 H, H-14), 0.81 (s, 3 H, H-11), 0.77 (s, 3 H, H-12); ^{13}C NMR (50 MHz, C_6D_6) δ 235.8 (CO), 112.6 (C-10a), 104.6 (C-8a), 99.5 (C-8), 96.2 (C-6), 87.6 (C-5), 80.9 (C-7), 48.2 (C-4a), 47.2 (C-9a), 45.9 (C-4), 39.0 (C-2), 34.1 (C-9), 32.8 (C-13), 30.7 (C-3), 30.1 (C-14), 28.9 (C-11), 24.5 (C-12), 21.0 (C-1), 16.6 (C-15); IR (KBr) 3419 (s, ν_{NH}), 2967 (m), 2950 (s), 2923 (m), 2904 (m), 1928 (vs, ν_{CO}), 1860 (vs, ν_{CO}), 1849 (vs, ν_{CO}), 1822 (vs, ν_{CO}), 1553 (s), 1496 (m), 678 (s), 639 (s) cm^{-1}; ME (EI) *m/e* 393 (M, 21), 309 (100), 257 (48), 256 (62), 242 (86), 158 (53), 118 (28), 107 (32), 91 (23), 52 (88); HRMS calcd for $C_{21}H_{27}NO_3Cr$ 393.1396, found 393.1391. Anal. Calcd for $C_{21}H_{27}NO_3Cr$: C, 64.10; H, 6.92; N, 3.52. Found: C, 64.29; H, 7.26; N, 3.29.

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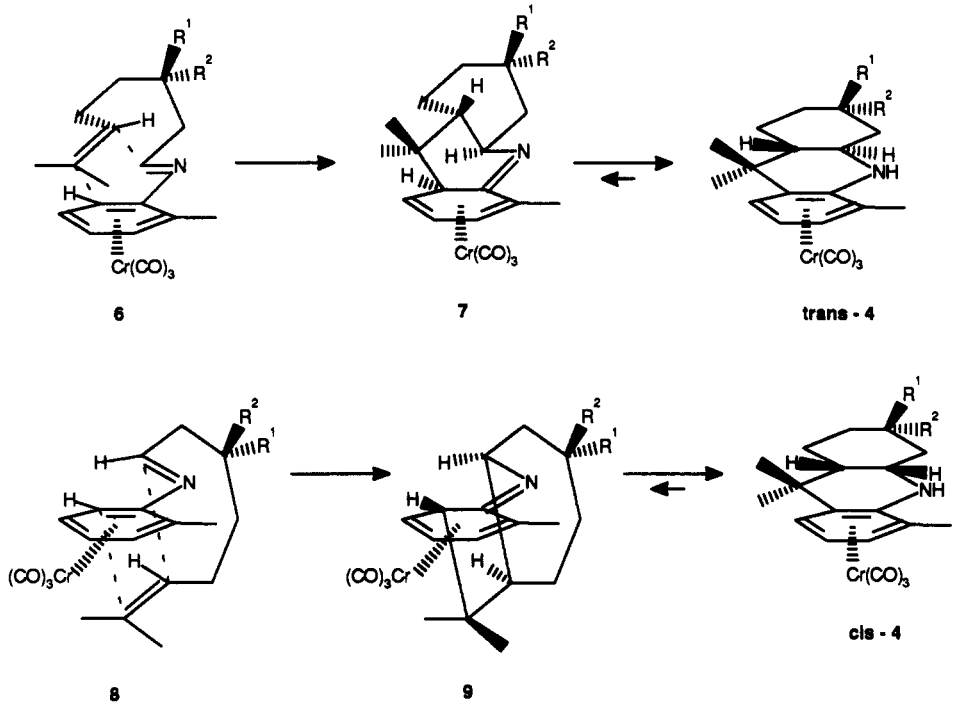
(16) Due to trace amounts of paramagnetic CrO_3, which could not be completely removed from the NMR sample, the signals of the aromatic protons appear as broad multiplets.

Scheme II



Tricarbonyl[*trans*-(3*R*)-3,5,9,9-tetramethyl-1,2,3,4,-4a,9,9a,10-octahydroacridine]chromium (4b). Flash chromatography yielded 292 mg (77%) of yellow crystals: mp 156 °C dec; $[\alpha]_D^{20}$ = +123.3° (*c* = 1.20; $CHCl_3$); ^1H NMR (200 MHz, C_6D_6) δ 5.17 (d, *J* = 6 Hz, 1 H, H-6), 4.95 (d, *J* = 6 Hz, 1 H, H-8), 4.19 (t, *J* = 6 Hz, 1 H, H-7), 3.24 (s, broad, 1 H, NH), 2.85 (ddd, *J* = 15 Hz, *J* = 11 Hz, *J* = 4 Hz, 1 H, H-4a), 1.53 (s, 3 H, H-14), 1.52–0.92 (m, 6 H, H-4eq, H-9a, H-3, H-2eq, H-1), 1.18 (s, 3 H, H-12), 0.85 (s, 3 H, H-13), 0.73 (d, *J* = 9 Hz, 3 H, H-11), 0.92–0.72 (m, 2 H, H-4ax, H-2ax); ^{13}C NMR (50 MHz, C_6D_6) δ 235.8 (CO), 112.5 (C-10a), 104.7 (C-8a), 99.4 (C-8), 96.2 (C-6), 87.5 (C-5), 80.9 (C-7), 50.1 (C-4a), 47.5 (C-9a), 42.0 (C-4), 34.8 (C-2), 34.1 (C-9), 30.5 (C-12), 30.1 (C-13), 28.8 (C-3), 24.7 (C-1), 22.1 (C-11), 16.6 (C-14); IR (KBr) 3419 (m, ν_{NH}), 2963 (s), 2924 (m), 2868 (m), 1945 (vs, ν_{CO}), 1853 (vs, ν_{CO}), 1838 (vs, ν_{CO}), 1543 (m), 1261 (s), 1091 (s), 1020 (s), 799 (vs) cm^{-1}; MS (EIF) *m/e* 379 (M, 13), 323 (25), 295 (100), 243 (48), 242 (69), 228 (62), 158 (42), 91 (21), 69 (50), 55 (52), 52 (81); HRMS calcd for $C_{20}H_{25}NO_3Cr$ 379.1240, found 379.1233. Anal. Calcd for $C_{20}H_{25}NO_3Cr$: C, 63.31; H, 6.64; N, 3.69. Found: C, 63.28; H, 6.89; N, 3.52.

Tricarbonyl(*trans*-5,9,9-trimethyl-1,2,3,4,4a,9,9a,10-octahydroacridine]chromium (4c). Flash chromatography yielded 150 mg (41%) of yellow crystals: mp 150 °C dec; ^1H NMR (200 MHz, C_6D_6) δ 5.19 (d, *J* = 6 Hz, 1 H, H-8), 4.97 (d, *J* = 6 Hz, 1 H, H-6), 4.20 ("t", *J* = 6 Hz, *J* = 6 Hz, 1 H, H-7), 3.30 (s, broad, 1 H, NH), 2.86 (m, broad, 1 H, H-4a), 1.52 (s, 3 H, H-13), 1.18 (s, 3 H, H-11), 0.86 (s, 3 H, H-12), 1.52–0.91 (m, 9 H, H-1, H-2, H-3, H-4, H-9a); ^{13}C NMR (50 MHz, C_6D_6) δ 235.9 (CO), 128.9 (C-10a), 104.6 (C-8a), 99.5 (C-8), 96.3 (C-6), 87.5 (C-5), 80.9 (C-7), 50.4 (C-4a), 47.8 (C-9a), 34.1 (C-9), 33.7 (C-4), 30.1 (C-11), 28.6 (C-12), 26.2 (C-2), 24.9 (C-3), 24.2 (C-1), 16.6 (C-13); IR (KBr) 3405 (m, ν_{NH}), 2968 (w), 2959 (w), 2931 (m), 2858 (w), 1955 (s, ν_{CO}), 1934 (s, ν_{CO}), 1857 (vs, ν_{CO}), 1825 (vs, ν_{CO}), 1541 (m), 1506 (m), 1485 (m), 1359 (m), 654 (m), 641 (m), 633 (m) cm^{-1}; MS (EI) *m/e* 365 (M, 18), 309 (21), 281 (100), 228 (67), 214 (58), 184 (25), 158 (43), 144 (35), 113 (29), 97 (29), 85 (47), 83 (47), 71 (42), 69 (50), 57 (81), 52 (94); HRMS calcd for $C_{19}H_{23}NO_3Cr$ 365.1083, found 365.1090. Anal. Calcd for $C_{19}H_{23}NO_3Cr$: C, 62.45; H, 6.35; N, 3.83. Found: C, 62.43; H, 6.33; N, 3.55.

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Supplementary Material Available: Details of the X-ray crystal structure determination of **4a**, including tables of crystal data and refinement details, positional parameters for H atoms, thermal parameters, and additional bond distances and angles (8 pages). Ordering information is given on any current masthead page.

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