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SOME NEW ARENE-CHROMIUM DICARBONYL CHELATES

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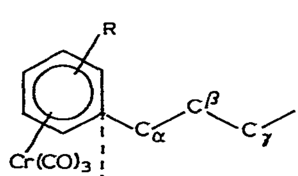
Summary

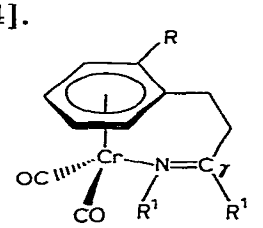
The photochemical synthesis, spectroscopic properties (IR, ^1H NMR, ^{13}C NMR) and X-ray structure of some novel chromium(0) dicarbonyl chelates are described.

Introduction

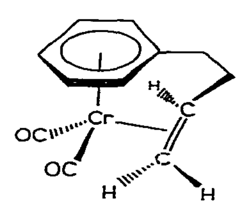
Thermodynamically and kinetically controlled asymmetric transformations are important methods for producing optically active compounds [1]. However, at room temperature values $\Delta\Delta G^0$ and $\Delta\Delta G^{\neq}$ of about 3 kcal/mol are necessary to approach almost complete asymmetric induction, and the question of how can one create such free energy differences between diastereomeric species (products or transition states) from steric, electronic and dipolar factors is still a challenge. In the course of our studies on asymmetric synthesis using chiral arenechromium tricarbonyl complexes I to induce chirality [2,3] we observed that ~100% asymmetric induction could be obtained during reactions at C^α and/or C^β, but only if the aromatic ring is *ortho*-substituted and the incoming group is sufficiently large. Hence no asymmetric induction is observed for reactions performed at C^γ [4].



(I, chiral inducer)



(II)



(III)

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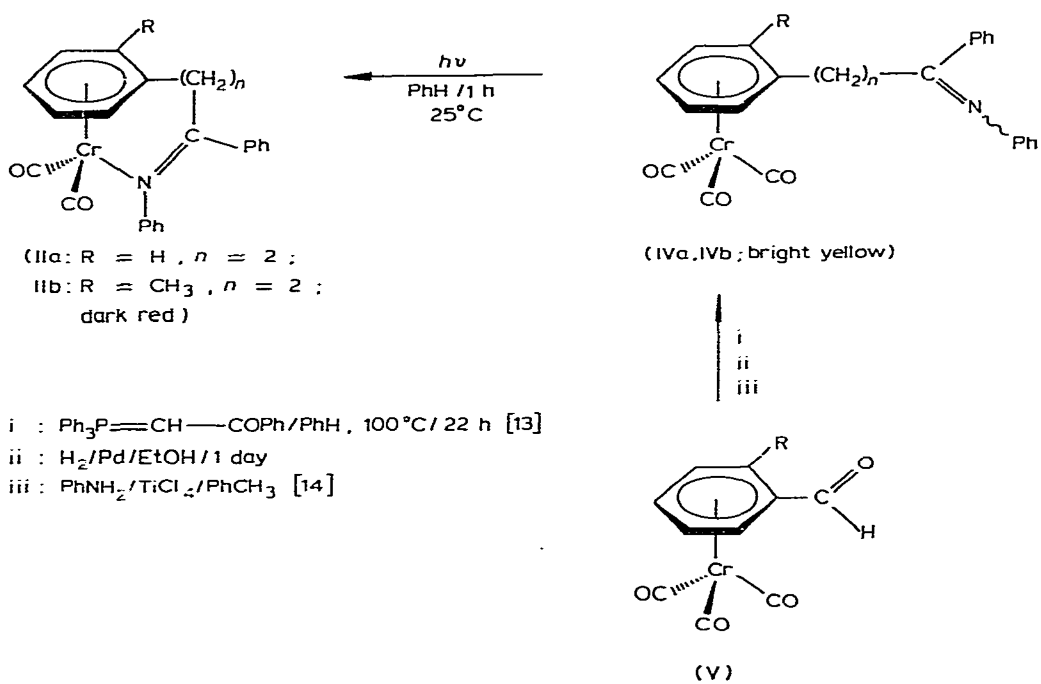
Arenechromium dicarbonyl chelates (II) in which the γ-carbon undergoing the reaction is held close to the chiral auxiliary could be expected to lead to higher degree of asymmetric induction and they, indeed, do so [4,5]. However, the only chelates described in the literature up to now are of type III [6a—6d]. We report in this paper the synthesis, molecular structure and spectral properties of a new type of chelate II.

Results

The synthesis of chelates IIa—IIc, Scheme 1, was accomplished by irradiation

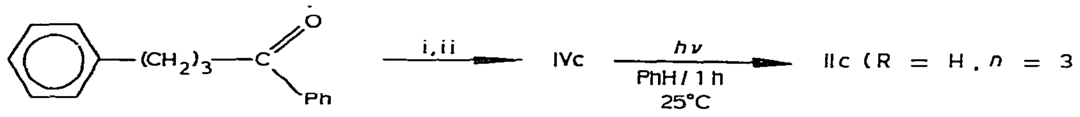
SCHEME 1



of the arenechromium tricarbonyl complexes IVa—IVc under nitrogen using a high pressure mercury lamp and anhydrous benzene as solvent. On irradiation the bright yellow color of the starting compounds IVa—IVc disappears rapidly, giving a dark-red color characteristic of all the chelates. The reaction can be followed by infrared spectroscopy because the two carbonyl absorptions, $\nu(C\equiv O)$, at ~1965 and ~1890 cm^{-1} of the starting tricarbonyl complexes are replaced by two carbonyl absorptions at ~1890 and ~1830 cm^{-1} (the reaction is complete in about 1 to 2 h). Complexes IVa—IVb were synthesized in a three-step reaction sequence from Va—Vb which, when chiral, as in Vb (R = Me), can be resolved easily [7]. Complex IVc, Scheme 2, was synthesized from ketone VI in a two-step reaction.

Chelate IIa was crystallized from a mixture of diethyl ether/hexane (70/30) at —30°C. The dark-red solution was concentrated slowly by passing nitrogen through the flask to give a few dark-red single crystals suitable for X-ray

SCHEME 2



(VI)

i : $Cr(CO)_6$ n Bu_2O/ Heptane 150°C
ii : $PhNH_2/TiCl_4/PhCH_3$ [14]

studies [8]. The structure of IIa is shown in Fig. 1 and 2. It appears that the dark-red compound obtained is a monomer and has the expected chelated structure. The $Cr(CO)_2(C{=}N)$ group adopts a conformation intermediate between staggered and C(1)C(3)C(5)-eclipsed forms (Fig. 2). The azomethine double bond is slightly distorted, the chromium atom being out of the

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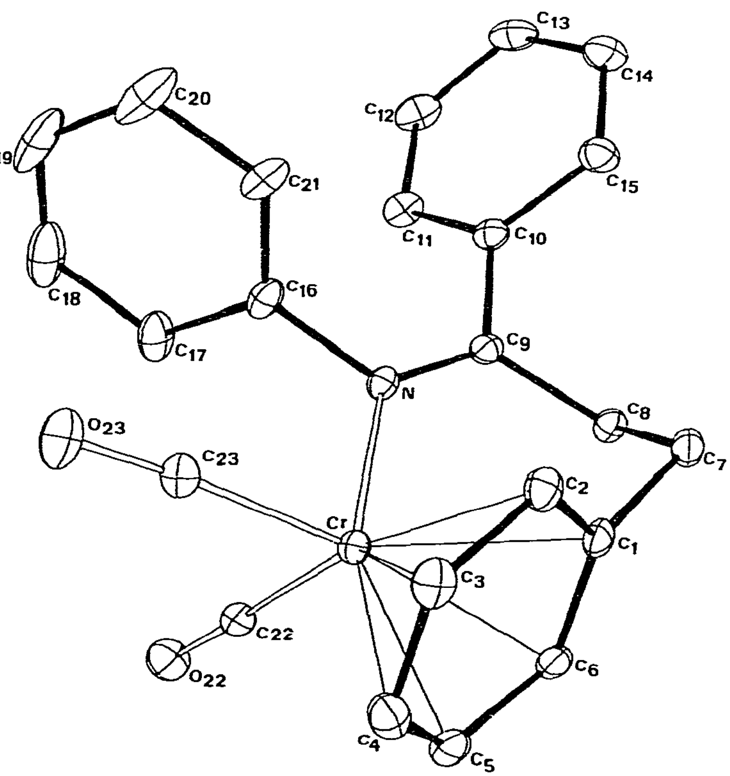
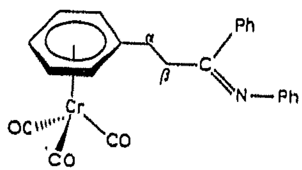


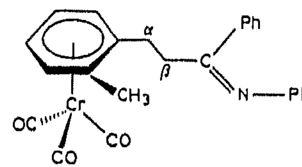
Fig. 1. ORTEP drawing of $Cr(CO)_2C_6H_5(CH_2)_2C(Ph){=}N(Ph)$. All atoms are represented by 50% probability thermal ellipsoids. Main distances (Å) are Cr—C(1), 2.211(3); Cr—C(2), 2.198(3); Cr—C(3), 2.190(3); Cr—C(4), 2.206(3); Cr—C(5), 2.172(3); Cr—C(6), 2.215(3); Cr—N, 2.121(2); Cr—C(22), 1.843(3); Cr—C(23), 1.831(3); C(1)—C(2), 1.416(4); C(2)—C(3), 1.408(5); C(3)—C(4), 1.387(5); C(4)—C(5), 1.399(5); C(5)—C(6), 1.414(5); C(6)—C(1), 1.404(4); C(1)—C(7), 1.492(4); C(7)—C(8), 1.526(2); C(8)—C(9), 1.508(4); C(9)—N, 1.296(4); C(9)—C(10), 1.497(4); N—C(16), 1.443(4). Main angles (deg) are Cr—N—C(9), 130.8(2); Cr—N—C(16), 112.6(2); C(9)—N—C(16), 116.3(2).

TABLE 1

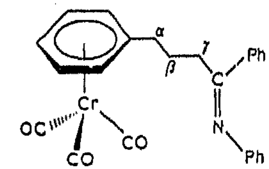
SPECTRAL PROPERTIES OF COMPOUNDS IIa–IIc AND OF IVa–IVc FOR COMPARISON



	ν(C=N)	ν(C=O)		
IR [a] (C_6H_6)	1625	1965 1885		
	Ring A ($AA'BB'C$)	$H^{\alpha,\beta}$ ($XX'YY'$)		
^{1}H NMR [b] (acetone-d_6)	*o* ~5.15(m) *m, p* ~5.5(m)	~2.6(m) ~2.95(m)		
	Ring A	$C^{\alpha,\beta}$	C=N	C=O
^{13}C NMR [c] (C_6D_6)	1 117.17 2–6 93.15 3–5 92.23 4 90.39	α 33.11 β 30.74	166.4	232.2

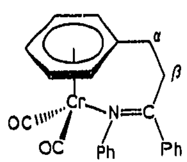


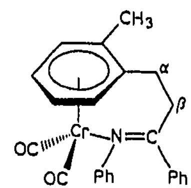
	ν(C=N)	ν(C=O)			
IR [a] (C_6H_6)	1628	1965 1890			
	Ring A (ABCD)	$H^{\alpha,\beta}$ (VXYZ)	CH_3		
^{1}H NMR [b] (acetone-d_6)	~5.40(m)	~2.85(m)	1.82(s), 3H		
	Ring A	$C^{\alpha,\beta}$–CH_3		C=N	C=O
^{13}C NMR [c] (C_6D_6)	1 109.36 2 94.50 3 91.11 4 92.58 5 94.56 6 107.83	α 30.00 β 30.91 CH_3 17.70		166.35	233.7

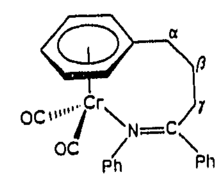


	ν(C=N)	ν(C=O)		
IR [a] (C_6H_6)	1630	1970 1895		
	Ring A ($AA'BB'C$)	$H^{\alpha,\beta,\gamma}$ ($AA'BB'CC'$)		
^{1}H NMR [b] (acetone-d_6)	*o* ~5.15(m) *m,p* ~5.4(m)	β ~ 1.90(m) α,γ ~ 2.2, 3.8(m)		
	Ring A	$C^{\alpha,\beta,\gamma}$	C=N	C=O
^{13}C NMR [c] (C_6D_6)	1 113.16 2–6 94.54 3–5 92.71 4 90.62	α 35.30 β,γ { 29.98 29.83	168.45	233.76

TABLE 1 (continued)







	ν(C=N)	ν(C=O)			ν(C=N)	ν(C=O)			ν(C=N)	ν(C=O)		
IR [d] (C_6H_6)	*e*	1890 1830			*e*	1885 1828			*e*	1888 1830		
	Ring A	$H^{\alpha,\beta}$			Ring A	$H^{\alpha,\beta}$	CH_3		Ring A	$H^{\alpha,\beta,\gamma}$		
^{1}H NMR (acetone-d_6)	*o* 5,38 d, 2H *m* 4,70 t, 2H *p* 3,47 t, 1H ^3J 6 Hz	3,30—2,30 m, 4H			*o* 5,32 d, 1H m_1 4,75 t, 1H m_2 4,16 d, 1H *p* 3,77 t, 1H ^3J 6 Hz	3,45—2,20 m, 4H	2,37 s, 3H		*o* 5,47 d, 2H *m* 5,00 t, 2H *p* 3,77 t, 1H ^3J 6 Hz	3,10—1,50 m, 6H		
	Ring A	$C^{\alpha,\beta}$	C=N	C=O	Ring A	$C^{\alpha,\beta}$—CH_3	C=N	C=O	Ring A	$C^{\alpha,\beta,\gamma}$	C=N	C=O
^{13}C NMR (C_6D_6)	1 107,36 2—6 89,35 3—5 91,24 4 78,45	α 42,86 β 29,24	182,24	241,63	1 106,3 2 103,2 3 98,2 4 80,5 5 88,8 6 87,1	α 44,90 β 25,70 CH_3 17,93	182,19	242,4	1 106,8 2—6 90,44 3—5 91,24 4 78,12	α 40,31 β 20,80 γ 30,33	184,04	240,23

[a] Perkin—Elmer 257. [b] Perkin—Elmer R24/A 60 MHz. [c] Cameca 250. [d] Cells are made of ITRAN 2. [e] No absorption band in the zone 1600—1650 cm^{-1}

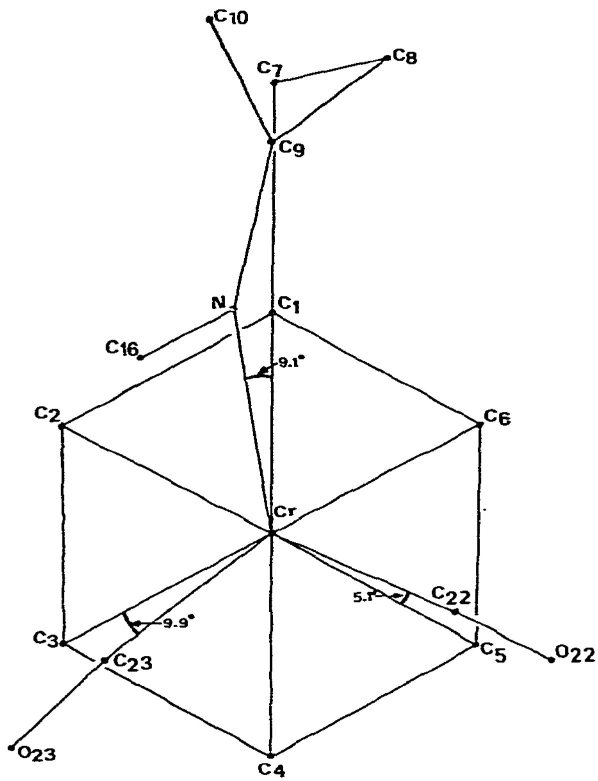


Fig. 2. Projection of atoms out of the benzene ring plane. The two phenyl groups were omitted for clarity. Main angles (deg) are C(1)—C(2)—C(3), 119.6(3); C(2)—C(3)—C(4), 121.2(3); C(3)—C(4)—C(5), 119.4(3); C(4)—C(5)—C(6), 120.6(3); C(5)—C(6)—C(1), 119.7(3); C(6)—C(1)—C(2), 119.4(3).

C(10)C(9)N plane by —0.26 Å and the C(16) carbon atom by +0.06 Å.

The aromatic rings B and C are, as expected for *cis*-diphenylimine [9], twisted out of the plane of the double bond. The Cr—N bond length, 2.121 Å, is within experimental error equal to the sum of the single-bonded covalent radii (Cr, 1.46 Å [10]; N, 0.70 Å [11]). The C=N bond, 1.296 Å is only slightly longer in the chelation than the sum of the double-bonded covalent radii, 1.265 Å [11].

The complexed aromatic ring can be regarded as planar, carbons C(1) and C(4) being +0.013 Å and —0.033 Å, respectively, out of the plane of carbons C(2)C(3)C(5)C(6), but carbon C(7) is 0.124 Å out of the mean plane of this aromatic ring. Some spectral properties of chelates IIa—IIc and, for comparison, of the starting complexes IVa—IVc are given in Table 1. It should be noted that the displacement of the IR carbonyl absorptions towards larger wavelength is consistent with the replacement in the chelates of one of the three C≡O ligands by a ligand, C=N, having a lower back-donating ability [12a—12c]. In the ^{1}H NMR spectrum the most important feature is the unusually large shielding, —1.5 to —2 ppm, of the aromatic proton *para* to the chain in the complexed ring in the chelates.

In the ^{13}C NMR the signal from the corresponding aromatic carbon *para* to the chain is also significantly shielded by ca. —12 ppm. The deshielding of +16 ppm for the azomethine carbons and of ~ +9 ppm for the carbonyl carbons is consistent with complexation of the azomethine group and replacement of one of the three carbonyls by a group having a lower back-donating ability. The large NMR shieldings of the proton and of the carbon *para* to the chain are not understood. These novel complexes are of considerable interest because their use leads to almost optically pure amines [4].

Experimental

Synthesis of complexes IVa and IVb

Wittig reaction. Triphenylphosphobenzoylmethylene was prepared according to the method described by Ramirez et al. [13]. A mixture of 0.011 mol of chromium tricarbonyl complex V and 0.012 mol of phosphorus ylide (4.5 g) in 150 ml of anhydrous benzene is heated under reflux for 22 h. (The reaction can be monitored by IR.) The solvent is evaporated and the complex chromatographed on silica gel 60 (70—230 mesh ASTM), eluent: ether/hexane 70/30.

Reduction of the double bond. Catalytic hydrogenation is performed in a usual Parr hydrogenator. To 3×10^{-3} mol of the relevant complex obtained from the Wittig reaction in 80 ml of ethanol are added ~100 mg of Pd/C; H_2 is introduced up to 50/psi, and this H_2 pressure is maintained during 22 h stirring. The ethanol is then evaporated and the residual complex chromatographed on silica gel 60 (70—230 mesh ASTM), eluent: ether/hexane 65/35.

Imine preparation. The Weingarten method is used [14]. In this 0.02 mol of the complexed ketone obtained from the two processes described above (or from complexation of VI, see below) and 0.06 mol of aniline in 50 ml of anhydrous toluene are stirred together at ambient temperature. Then 0.01 mol of $TiCl_4$ in 20 ml of anhydrous toluene is added dropwise, and the mixture is subsequently heated under reflux for 3 h. Titanium oxide is filtered off and the toluene is evaporated. The complex may be recrystallized by placing an ether/hexane solution (~60/40) in a refrigerator.

IVa: Global yield 54%, bright yellow solid, m.p. 78°C. Analysis Found: C, 67.75; H, 4.56; N, 3.16. $C_{24}H_{19}O_3NCr$ calcd.: C, 68.41; H, 4.54; N, 3.32%. IR, ^{1}H and ^{13}C NMR, see Table 1.

IVb: Global yield 44%, bright yellow solid, m.p. 98—99°C. Analysis Found: C, 68.96; H, 4.86; N, 3.38. $C_{25}H_{21}O_3NCr$ calcd.: C, 69.02; H, 4.86; N, 3.39%. $[\alpha]_D^{25}$ +42.2° (c = 0.2, $CHCl_3$) (starting from (+)-1*S*-Vb).

Synthesis of complexes IVc

Complexation. A mixture of 0.024 mol of diaromatic ketone VI, 0.024 mol of $Cr(CO)_6$ (5.3 g) is refluxed (150°C) in a mixture of 80 ml n-Bu_2O/120 ml n-heptane for 45 h in a Strohmeier apparatus (under nitrogen), and the solvents are then taken off in a rotary evaporator. The crude product is chromatographed (in fractions of 2 g) on silica gel 60 (70—230 mesh ASTM) (ϕ 30 mm, l 400 mm) with ether/hexane 70/30 as eluant.

Imine preparation (see above). IVc: Overall yield 30%, bright yellow solid, m.p. 68—69°C. Analysis. Found: C, 68—61; H, 4.78; N, 3.37. $C_{25}H_{21}O_3NCr$ calcd.: C, 69.02; H, 4.86; N, 3.39%. IR, ^{1}H and ^{13}C NMR, see Table 1.

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TABLE 2

FRACTIONAL ATOMIC COORDINATES AND FINAL STRUCTURE FACTORS [a] WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.18460(2)	−0.06885(9)	0.06637(3)	0.00056(0)	0.0138(1)	0.00212(2)	0.00013(5)	0.00046(1)	0.0011(1)
O(22)	0.20690(9)	0.2307(5)	−0.0475(2)	0.00111(3)	0.0260(8)	0.0043(1)	−0.0017(3)	0.0016(1)	0.0061(5)
O(23)	0.14019(11)	−0.2726(5)	−0.0919(2)	0.00151(4)	0.0295(9)	0.0034(1)	−0.0010(3)	0.0002(1)	−0.0055(6)
N	0.13815(9)	0.1145(4)	0.0788(2)	0.00059(3)	0.0119(7)	0.0023(1)	−0.0001(2)	0.00021(9)	0.0015(5)
C(1)	0.1971(1)	−0.1026(6)	0.2045(2)	0.00063(3)	0.0180(9)	0.0020(1)	0.0009(3)	0.0002(1)	0.0027(6)
C(2)	0.1809(1)	−0.2837(6)	0.1651(2)	0.00078(3)	0.0158(9)	0.0027(1)	−0.0003(3)	0.0005(1)	0.0031(6)
C(3)	0.1980(1)	−0.3795(6)	0.1079(3)	0.00103(4)	0.0142(9)	0.0032(2)	0.0013(3)	0.0006(1)	0.0013(7)
C(4)	0.2304(1)	−0.2996(7)	0.0893(2)	0.00096(4)	0.0217(10)	0.0032(2)	0.0033(4)	0.0012(1)	0.0033(7)
C(5)	0.2457(1)	−0.1175(7)	0.1261(3)	0.00059(3)	0.0252(11)	0.0033(2)	0.0014(3)	0.0005(1)	0.0049(7)
C(6)	0.2300(1)	−0.0217(6)	0.1859(2)	0.00054(3)	0.0194(10)	0.0027(1)	0.0002(3)	0.0001(1)	0.0015(6)
C(7)	0.1779(1)	0.0114(6)	0.2598(2)	0.00074(3)	0.0204(10)	0.0022(1)	0.0000(3)	0.0006(1)	0.0005(6)
C(8)	0.1652(1)	0.2194(6)	0.2238(2)	0.00063(3)	0.0179(9)	0.0026(1)	0.0005(3)	0.0004(1)	−0.0014(6)
C(9)	0.1331(1)	0.2119(6)	0.1431(2)	0.00053(3)	0.0146(8)	0.0027(1)	−0.0003(3)	0.0006(1)	0.0011(6)
C(10)	0.0960(1)	0.3109(6)	0.1450(2)	0.00061(3)	0.0154(9)	0.0032(2)	−0.0007(3)	0.0006(1)	−0.0024(6)
C(11)	0.0772(1)	0.4560(6)	0.0880(3)	0.00082(4)	0.0164(10)	0.0043(2)	0.0006(3)	0.0006(1)	0.0001(7)
C(12)	0.0424(1)	0.5362(7)	0.0951(3)	0.00078(4)	0.0198(11)	0.0061(2)	0.0024(4)	0.0003(2)	0.0021(9)
C(13)	0.0262(1)	0.4749(8)	0.1572(3)	0.00061(3)	0.0292(13)	0.0066(2)	0.0004(4)	0.0015(1)	−0.0036(10)
C(14)	0.0451(1)	0.3349(8)	0.2138(3)	0.00082(4)	0.0330(14)	0.0052(2)	0.0002(4)	0.0019(1)	−0.0009(10)
C(15)	0.0800(1)	0.2533(7)	0.2098(3)	0.00079(4)	0.0231(11)	0.0041(2)	0.0010(3)	0.0014(1)	0.0015(8)
C(16)	0.1058(1)	0.1111(6)	0.0046(2)	0.00067(3)	0.0169(9)	0.0029(2)	0.0015(3)	−0.0002(1)	−0.0014(6)
C(17)	0.1068(1)	0.2258(7)	−0.0654(3)	0.00127(5)	0.0274(12)	0.0028(2)	0.0053(4)	0.0003(2)	0.0042(8)

C(18)	0,0749(2)	0,2149(9)	—0,1367(3)	0,00206(7)	0,0391(15)	0,0031(2)	0,0096(5)	—0,0005(2)	0,0013(10)
C(19)	0,0442(2)	0,0958(10)	—0,1373(4)	0,00138(6)	0,0447(18)	0,0056(3)	0,0062(5)	—0,0032(2)	—0,0117(11)
C(20)	0,0436(2)	—0,0165(9)	—0,0687(4)	0,00102(5)	0,0309(14)	0,0080(3)	0,0014(5)	—0,0023(2)	—0,0125(11)
C(21)	0,0744(1)	—0,0102(7)	0,0034(3)	0,00073(4)	0,0212(10)	0,0046(2)	0,0003(4)	—0,0006(2)	—0,0031(8)
C(22)	0,1987(1)	0,1184(6)	—0,0022(2)	0,00058(3)	0,0200(10)	0,0028(1)	0,0002(3)	0,0006(1)	0,0009(6)
H(2)	0,1587(0)	—0,3413(0)	0,1777(0)	8,0000(0)					
H(3)	0,1872(0)	—0,5042(0)	0,0825(0)	8,0000(0)					
H(4)	0,2424(0)	—0,3679(0)	0,0518(0)	8,0000(0)					
H(5)	0,2672(0)	—0,0578(0)	0,1109(0)	8,0000(0)					
H(6)	0,2416(0)	0,0980(0)	0,2136(0)	8,0000(0)					
H(71)	0,1952(0)	0,0237(0)	0,3140(0)	8,0000(0)					
H(72)	0,1555(0)	—0,0617(0)	0,2637(0)	8,0000(0)					
H(81)	0,1870(0)	9,2866(0)	0,2136(0)	8,0000(0)					
H(82)	0,1566(0)	0,2949(0)	0,2648(0)	8,0000(0)					
H(11)	0,0880(0)	0,4972(0)	0,0426(0)	8,0000(0)					
H(12)	0,0298(0)	0,6411(0)	0,0559(0)	8,0000(0)					
H(13)	0,0016(0)	0,5289(0)	0,1594(0)	8,0000(0)					
H(14)	0,337(0)	0,2893(0)	0,2578(0)	8,0000(0)					
H(15)	0,0938(0)	0,1601(0)	0,2528(0)	8,0000(0)					
H(17)	0,1293(0)	0,3105(0)	—0,0652(0)	8,0000(0)					
H(18)	0,0733(0)	0,2882(0)	—0,1873(0)	8,0000(0)					
H(19)	0,0214(0)	0,0870(0)	—0,1861(0)	8,0000(0)					
H(20)	0,0216(0)	—0,1038(0)	—0,0698(0)	8,0000(0)					
H(21)	0,0738(0)	—0,0878(0)	0,0534(0)	8,0000(0)					

[a] The form of the anisotropic thermal parameter is $\exp\left\{-(B^{\star}_{1,1}h^2 + B^{\star}_{2,2}k^2 + B^{\star}_{3,3}l^2 + B^{\star}_{1,2}hk + B^{\star}_{1,3}hl + B^{\star}_{2,3}kl)\right\}$.

Synthesis of chelates IIa—IIc: Photocyclization

Irradiation of the complexed imines IVa—IVc is carried out under nitrogen using a high-pressure mercury lamp (Philips HPK 125 W). The vessel is a standard Pyrex photolysis system with a water-cooled jacket and equipped with a septum cap and needles to allow continuous bubbling of nitrogen through the solution (which provides stirring during photolysis) and to allow filtration under an inert atmosphere when the reaction is complete. By adjusting the positions of the needles the solution may be forced through a filtration funnel to remove traces of chromium oxide, if any is present, into a round bottom flask flushed with nitrogen. The solution is finally evaporated to dryness under vacuum.

Irradiation is carried out with 5×10^{-4} mol of imines IVa—IVc in 100 ml of degassed benzene. The bright yellow color of the starting complex rapidly turns dark-red (the usual color of this type of chelate). The reaction can be monitored by IR spectroscopy and is complete within 1 or 2 h.

IIa. Yield 100%, dark-bloodish red solid, decomposes. IR, X-ray, ^{1}H and ^{13}C NMR, see Table 1 and text.

IIb. Yield 100%, dark-red solid, decomposes. IR, ^{1}H and ^{13}C NMR, see Table 1.

IIc. Yield 100%, dark-red solid, decomposes. IR, ^{1}H and ^{13}C NMR, see Table 1.

Supplementary material available. Complete listings of atomic coordinates and thermal parameters (Tables I and II) and computed and observed structure factor amplitude (Table III) are available on request. In Table 2 are given fractional atomic coordinates and final structure factors.

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