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Synthesis of organic heterocycles via multicomponent reactions with cyano transition metal complexes ☆

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Abstract

Twenty three complexes of the type $[\mathrm{M(CO)_5\overline{CNC(NHR^1)C(R^2)(R^3)O}}]$ (**1–23**) have been synthesized by the three-component cycloaddition (3CC) of $[\mathrm{M(CN)(CO)_5}]^-$ (M = Cr, Mo, W) with various isocyanides $\mathrm{CNR^1}$ ($\mathrm{R^1}$ = Me, Cy, ^{t}Bu, *p*-Tol, $\mathrm{CH_2CO_2Et}$ and $\mathrm{CH_2SO_2Tol}$-*p*) and carbonyl compounds $\mathrm{R^2R^3C{=}O}$ ($\mathrm{R^2}$, $\mathrm{R^3}$ = for example, Me, Me; Et, Et; ^{t}Bu, Me; H, ^{i}Pr; $\mathrm{CF_3}$, $\mathrm{CF_3}$; $\mathrm{[CH_2]_4}$; $\mathrm{[CH_2]_5}$). Several other mono- and di-cyano complexes ($[\mathrm{Mn_2(CN)(CO)_9}]^-$, $[\mathrm{Fe(CN)_2Cp(CO)}]^-$, [Fe(CN)Cp(dppe)], [Ru(CN)Cp(dppe)] and $[\mathrm{Co(CN)_2(dmgH)_2}]^-$) also undergo this obviously general reaction resulting in the 4-amino-oxazolin-2-ylidene complexes $[\mathrm{Mn_2(CO)_9\{\overline{CNC(NH^tBu)C(Me_2)O}\}}]$ (**30**), $[\mathrm{MCp\{\overline{CNC(NH^tBu)C(Me_2)O}\}dppe](BF_4)}$ [M = Fe (**34**), Ru (**35**)] and $[\mathrm{Co(CN)(dmgH)_2\{\overline{CNC(NHCy)C(Me_2)O}\}}]$ (**36**).

With amine hydrochloride as the fourth component, however, the 4CC products $[\mathrm{Mn_2(CO)_9\{\overline{CN(H)C(NH^tBu)C(Ph)N}Ph\}}]$ (**29**), $[\mathrm{Fe(CN)Cp\{\overline{CN(H)C(NH^tBu)C(Ph)N}Ph\}CO}]$ (**31**) and $[\mathrm{Co(CN)(dmgH)_2\{\overline{CN(H)C(NHR^1)C(R^2)N}Ph\}}]$ [$\mathrm{R^1}$ = Cy, $\mathrm{R^2}$ = Ph (**37**); *p*-Tol (**38**); $\mathrm{R^1}$ = ^{t}Bu, $\mathrm{R^2}$ = *p*-Tol (**39**)] have been obtained on using a molar ratio of cyano complex/organic reagents of 1:2, afforded the bis(heterocyclic) complexes $[\mathrm{FeCp(CO)\{\overline{CN(H)C(NH^tBu)C(^iPr)N}H\}_2](PF_6)}$ (**32**), $[\mathrm{FeCp(CO)\{\overline{CNC(NH^tBu)C(Me_2)O}\}_2](BF_4)}$ (**33**) and $[\mathrm{Co(dmgH)_2\{\overline{CN(H)C(NHCy)C(Ph)N}Ph\}_2][Co(CN)_2(dmgH)_2]}$ (**40**).

To confirm the claimed nature of the products, X-ray structure analyses have been carried out on $[\mathrm{Cr(CO)_5\{\overline{CNC(NHR^1)C(R^2)(R^3)O}\}}]$ (**9**) and $[\mathrm{Cr(CO)_5\{\overline{CN(H)C(NHR^1)C(R^2)N}R^3\}}]$ (**27**).

Detachment of the carbenoid 4-amino-imidazoles from the complexes $[\mathrm{M(CO)_5\{\overline{CN(H)C(NHR)C(Ph)N}Ph\}}]$ [M = W, R = Cy (**46**); M = Cr, R = ^{t}Bu (**47**)] by oxidation with $\mathrm{KMnO_4/Fe(NO_3)_3}$ surprisingly gave the 4-amino-5-*hydroxy*imidazol-2-ones **48** and **49** which were characterized by X-ray analyses.

Keywords: Multicomponent reaction; Organic heterocycles; Cyano complexes

1. Introduction

Through the use of cyanic acid (HOCN) or thiocyanic acid (HSCN) as acid components in four-component condensation reactions with isocyanides, aldehydes and primary amines (4CC), Ugi et al. opened an attractive synthetic access to five-membered heterocycles of the hydantoin type, viz. hydantoin-4-imides and 2-thiohydantoin-4-imides [1]. Such compounds are potentially biologically and pharmacologically active substances for whose synthesis numerous procedures have been developed including those via organometallics [2,3]. Stimulated by the isolobal analogy between an oxygen atom and an $\mathrm{ML_5}$–$\mathrm{d^6}$-transition metal complex fragment [4], we have started to look at 4CCs with hydrogen isocyanide complexes [e.g. $\mathrm{HNCM(CO)_5}$, M = Cr0, Mo0, W0] in the place of HNCO and have found a surprisingly general route to metal–carbon-bonded imidazoles carrying amino substituents in the 4-position (Scheme 1).

During the course of these investigations, a further novel reaction of the coordinated cyanide was discovered. This three-component [2 + 1 + 2] cycloaddition with one molecule each of isocyanide and ketone ('3CC') leads to complexes containing some kind of

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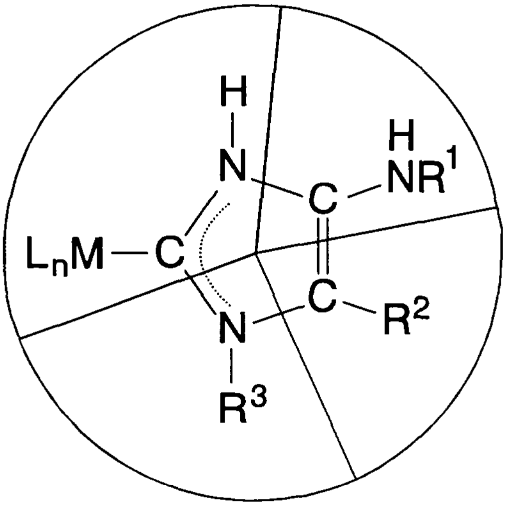


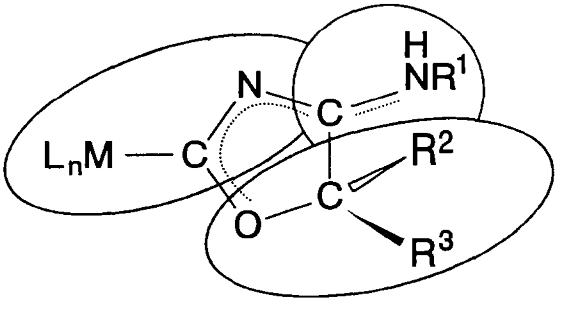
Scheme 1.

carbenoid non-aromatic 4-amino-oxazoline ligands (Scheme 2). Although lacking an organic precedent, this one-pot synthesis has turned out to be of a similar variability as the 4CC regarding the range of components tolerated.

A preliminary account has appeared on the 3CC reaction while organometallic 4CCs with pentacarbonyl(cyano)chromate, -molybdate and -tungstate have already been dealt with in a full paper [5,6]. Here we present the experimental, spectroscopic and structural details of in total 27 3CC and seven 4CC products with the main emphasis on both being the variation of the cyanometal complex and the different methods of cleaving the metal–carbene bond which determine the nature of the 'free' heterocyclic species.

Multicomponent one-pot reactions in general and 'tandem' or 'domino' processes, in particular, presently enjoy great popularity in the development of new synthetic strategies for natural products of biological relevance [7,8]. In organometallic chemistry, however, comparable reaction sequences are still scarce though not unknown. An efficient and elegant synthetic entry to six-membered carbocycles in natural products which benefits from the template effect of the central chromium atom and the high electrophilicity of the alkoxy(aryl) or alkoxy(alkenyl)-carbene ligands was devised in the early 1970s by Dötz et al. [9]. More recently, *N*-heterocycles have also become accessible by similar reaction patterns [10].

A different route to various azetidines, pyrroles, indoles, imidazolines and oxazolidines consisting of the combination of Fischer-type carbene complexes and isocyanides with or without a third component has been adopted by Aumann and coworkers [3,11,12]. Although proceeding in two steps via intermediate keteneimine ('NCC') complexes, these syntheses bear a strong resemblance to the chemistry reported here. Even more closely related are the novel two-step 2*H*-pyrrole syntheses from 'activated' aminocarbene ('CNC') moieties and polar alkynes [13]. Actually, all three synthetic approaches via transition metal complexes are complementary as regards the substitution pattern and regiochemistry of the resulting *N*-heterocycles.



Scheme 2.

2. Results and discussion

2.1. Three-component cycloadditions with pentacarbonyl(cyano) Group 6 metallates

A series of bright yellow complexes (**1–23**) has been synthesized via the three-component reactions of the hydrogenisocyanide complexes $M(CO)_5CNH$ (M = Cr, Mo, W) with isocyanides and carbonyl compounds, the latter at the same time serving as a solvent [1] [Eq. (1)]. The compounds **1–23** show a high thermal stability both in the solid state and in solution.

The reactions proceeded less smoothly with aldehydes as carbonyl components, which presumably is a consequence of their strong tendency for acid-promoted self-condensation. Note, however, that this is in marked contrast to the organometallic 4CC which only works with aldehydes [6].

Some ketones such as benzophenone, acetophenone and methyl vinyl ketone do not follow the 3CC reaction course. Thus, while arylketones only gave rise to undefined products, a competitive reaction took place in the case of the enone **24** by which the γ-oxo-alkylisocyanide complex **25** was formed [Eq. (2)]. Several complexes with this type of ligand including the one isolated here have already been reported [14,15].

Apart from this, there are practically no limits to variations of the carbonyl component. With cyclic ke-

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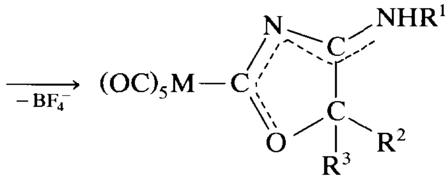
[1] Fortunately, replacing $M(CO)_5CNH$ by the parent cyano complexes $[M(CN)(CO)_5]^-$ plus an equivalent amount of HBF_4 proved to be of similar efficiency yet much more convenient.

$[M(CN)(CO)_5]^- + HBF_4 + CNR^1 + R^2R^3C{=}O$



(1)

1–23

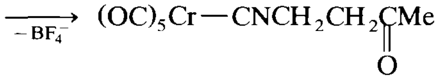
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
M	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr
R^1	Me	^{t}Bu	Cy	CH_2CO_2Et	*p*-Tol	CH_2SO_2Tol-*p*	^{t}Bu	^{t}Bu
R^2	Me	Me	Me	Me	Me	Me	Et	^{n}Bu
R^3	Me	Me	Me	Me	Me	Me	Me	Me

	9	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
M	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr	W
R^1	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Cy	Me
R^2	^{n}Hex	^{i}Bu	^{t}Bu	^{i}Pr	CF_3				Me
						$[CH_2]_4$	$[CH_2]_5$	$[CH_2]_5$	
R^3	Me	Me	Me	H	CF_3				Me

	18	**19**	**20**	**21**	**22**	**23**
M	W	W	W	W	W	Mo
R^1	^{t}Bu	Me	Cy	^{t}Bu	Cy	^{t}Bu
R^2	Me	$(CH_2)_2COMe$	Et		Ph	Me
				$[CH_2]_5$		
R^3	Me	Me	Et		H	Me

$[Cr(CN)(CO)_5]^- + H_2C{=}CHC(O)Me + HBF_4$

24



$$\xrightarrow[-BF_4^-]{} (OC)_5Cr{-}CNCH_2CH_2\underset{\displaystyle O}{\overset{}{C}}Me \qquad (2)$$

25

tones, spiro-heterocyclic compounds are obtained which are of particular interest because of their biological activity. Very remarkably, hexafluoroacetone could also be incorporated into the oxazoline ring to give complex **13**. No twofold 3CC has been achieved, however, with 2,5-hexanedione; again, only the mono product **19** was isolated.

Both non-functional and functional (TOSMIC, $CNCH_2CO_2Et$) isocyanides proved to be appropriate reagents for 3CCs. This is not true, however, of trimethylsilyl cyanide which is known to readily isomerize to the corresponding isocyanide; here, only the starting material was re-isolated.

As has already been pointed out, there is ample spectroscopic evidence for the chosen formulation of the products **1–23** as complexes of carbenoid non-aromatic 4-amino-oxazolines with an unprecedented π-delocalization along the O–C–N–C–NHR chain. In the high frequency region, the IR spectra are dominated by intense sharp ν(NH) bands over the range 3400–3300 cm^{-1}, particularly low-lying ν(CO) (E) and axial-(A_1) absorptions with their lowest components having dropped to 1850 cm^{-1}, and a strong band at ca. 1600 cm^{-1} accompanied by a less intense absorption somewhat above 1500 cm^{-1} (Table 1). The latter two

Table 1
Selected IR data (KBr) (cm^{-1}) for the complexes **1–23**

Complex	ν(NH)	ν(CO)	Others [a]
1	3379 (s)	2062 (m); 1941 (vs); 1876 (vs)	1638 (s); 1515 (m); 1508 (m)
2	3363 (s)	2061 (m); 1935 (vs); 1866 (vs)	1611 (s); 1518 (m); 1510 (m)
3	3358 (s)	2061 (s); 1918 (vs); 1859 (vs)	1623 (s); 1514 (m)
4	3303 (s)	2057 (s); 1925 (vs); 1904 (vs); 1719 (s)	1629 (s); 1521 (s)
5	3394 (m)	2066 (s); 1986 (s); 1918 (s); 1885 (s)	1713 (s); 1504 (m)
6	3248 (s)	2064 (s); 1970 (vs); 1913 (vs)	1718 (s); 1594 (m)
7	3366 (s)	2059 (m); 1979 (s); 1959 (vs); 1916 (vs); 1879 (vs)	1604 (s); 1513 (m)
8	3364 (s)	2059 (m); 1924 (vs); 1876 (vs)	1608 (s); 1514 (m)
9	3357 (s)	2060 (m); 1918 (vs); 1851 (vs)	1610 (s); 1513 (m)
10	3361 (s)	2060 (m); 1929 (vs); 1861 (vs)	1608 (s); 1517 (m)
11	3376 (s)	2060 (m); 1940 (vs); 1850 (vs)	1598 (s); 1505 (m)
12	3360 (s)	2060 (m); 1979 (s); 1933 (vs); 1874 (vs)	1615 (s); 1512 (m)
13	3386 (s)	2066 (s); 1986 (vs); 1955 (vs); 1930 (vs)	1611 (s); 1504
14	3356 (s)	2060 (m); 1932 (vs); 1878 (vs)	1609 (s); 1507 (m)
15	3358 (s)	2059 (s); 2002 (m); 1935 (vs); 1873 (vs)	1608 (s); 1509 (m)
16	3355 (s)	2061 (m); 1933 (vs); 1858 (vs)	1621 (s); 1504 (m)
17	3375 (s)	2068 (m); 1924 (vs); 1869 (vs)	1674 (s); 1514 (m)
18	3357 (s)	2067 (s); 1925 (vs); 1856 (vs)	1612 (s); 1516 (m)
19	3319 (s)	2065 (s); 1917 (s); 1919 (vs br); 1706 (s)	1643 (s); 1518 (m)
20	3349 (s)	2069 (s); 1978 (s); 1920 (vs br); 1845 (vs)	1619 (s); 1501 (s)
21	3352 (s)	1927 (s); 1867 (vs); 1852 (vs)	1734 (s); 1510
22	3359 (s)	2069 (s); 1975 (vs); 1918 (vs); 1876 (vs); 1848 (vs)	1661 (s); 1599 (m)
23	3367 (s)	2067 (s); 1933 (vs); 1858 (vs br)	1609 (s); 1514 (m); 1505 (m)

[a] Characteristic vibrations of the heterocyclic ligand.

bands have been assigned to the ν(N⋯C⋯O) motion, an IR feature highly characteristic of saturated cyclic N,O-carbenes [16] which in the present case is probably coupled to other ring vibrations (cf. Ref. [6]).

2.2. NMR spectra

The ^{13}C NMR chemical shifts of carbene carbon atoms are known to vary over quite wide ranges [17].

Table 2
^{1}H and ^{13}C NMR data for complexes **1–23** [a]

Complex	Solvent	^{1}H NMR	^{13}C NMR
1	DMSO-*d*$_6$	1.50 (s, 6H, CMe$_2$); 3.10 (s, 3H, Me); 9.98 (s, 1H, NH)	24.1 (C(*C*H$_3$)$_2$); 30.4 (*C*H$_3$); 87.1 (*C*Me$_2$); 182.7 (CN); 217.9 (CO$_{eq}$); 223.5 (CO$_{ax}$); 271.8 (carbene C)
2	DMSO-*d*$_6$	1.50 (s, 15H, CMe$_3$ + CMe$_2$); 9.38 (s, 1H, NH)	23.9 (C(*C*H$_3$)$_2$); 27.6 (C(*C*H$_3$)$_3$); 55.2 (*C*Me$_3$); 88.1 (*C*Me$_2$); 181.1 (CN); 217.9 (CO$_{eq}$); 233.6 (CO$_{ax}$); 271.8 (carbene C)
3	DMSO-*d*$_6$	1.22–2.00 (m, 10H, C$_6$H$_{10}$); 1.44 (s, 6H, CMe$_2$); 3.90 (br, 1H, *ipso*-H(Cy)); 9.74 (br, 1H, NH)	24.0 (C(*C*H$_3$)$_2$); 24.1, 24.7, 31.1, 53.5 (Cy); 87.1 (*C*Me$_3$); 181.4 (CN); 218.0 (CO$_{eq}$); 223.5 (CO$_{ax}$); 271.5 (carbene C)
4	DMSO-*d*$_6$	1.20 (t, 3H, OCH$_2$*C*H$_3$); 1.52 (s, 6H, CMe$_2$); 3.38 (br, 1H, NH); 4.16 (q, 2H, O*C*H$_2$Me); 4.36 (s, 2H, CH$_2$)	13.8 (OCH$_2$*C*H$_3$); 24.0 (C(*C*H$_3$)$_2$); 44.8 (*C*H$_2$); 61.0 (O*C*H$_2$Me); 88.1 (*C*Me$_3$); 167.5 (*C*OOEt); 183.2 (CN); 217.7 (CO$_{eq}$); 223.4 (CO$_{ax}$); 274.7 (carbene C)
5	DMSO-*d*$_6$	1.63 (s, 6H, CMe$_2$); 2.35 (s, 3H, PH–*C*H$_3$); 7.23–8.00 (m, 4H, Ph); 11.45 (s, br, 1H, NH)	20.4 (Ph–*C*H$_3$); 24.0 (C(*C*H$_3$)$_2$); 89.8 (*C*Me$_3$); 121.3, 129.4, 134.8, 135.8 (Ph); 178.8 (CN); 217.7 (CO$_{eq}$); 223.6 (CO$_{ax}$)
6	DMSO-*d*$_6$	1.38 (s, 6H, CMe$_2$); 2.48 (s, 3H, Ph–*C*H$_3$); 5.18 (d, 2H, CH$_2$); 7.38–7.85 (m, 4H, Ph); 11.05 (br, 1H, NH)	20.9 (Ph–*C*h$_3$); 23.7 (C(*C*H$_3$)$_2$); 63.2 (*C*H$_2$); 88.0 (*C*Me$_3$); 128.6, 129.6 (Ph); 217.4 (CO$_{eq}$)
7	DMSO-*d*$_6$	0.60 (t, 3H, CH$_2$*C*H$_3$); 1.50 (s, br, 12H, Me + CMe$_3$); 1.96 (q, 2H, *C*H$_2$CH$_3$); 9.38 (s, 1H, NH)	6.7 (CH$_2$*C*H$_3$); 23.0 (Me); 27.7 (C(*C*H$_3$)$_2$); 29.7 (*C*H$_2$CH$_3$); 55.3 (*C*Me$_3$); 91.7 (*C*(Et)(Me)); 180.0 (CN); 218.0 (CO$_{eq}$); 223.7 (CO$_{ax}$); 271.6 (carbene C)
8	DMSO-*d*$_6$	0.84 (t, 3H, CH$_2$*C*H$_3$); 1.00 (m 2H, CH$_2$*C*H$_2$Me); 1.26 (m, 2H, CH$_2$*C*H$_2$CH$_2$Me); 1.50 (s, 15H, Me + CMe$_3$); 1.92 (t, 2H, *C*H$_2$CH$_2$Me); 9.38 (s, 1H, NH)	13.4, 21.4, 24.3, 35.9 (^{n}Bu); 27.7 (C(*C*H$_3$)$_2$); 23.3 (Me); 55.3 (*C*Me$_3$); 91.2 (*C*(^{n}Bu)(Me)); 180.2 (CN); 218.0 (CO$_{eq}$); 223.7 (CO$_{ax}$)
9	DMSO-*d*$_6$	0.80–1.30 (m, 11H, (CH$_2$)$_4$Me); 1.50 (s, br, 12H, Me + CMe$_3$); 1.94 (t, 2H, *C*H$_2$CH$_2$^{n}Bu); 9.36 (s, 1H, NH)	13.6, 21.5, 21.9, 23.3, 30.7, 36.2 (^{n}Hex); 27.6 (C(*C*H$_3$)$_2$); 27.8 (Me); 55.2 (*C*Me$_3$); 91.2 (*C*(^{n}Hex)(Me)); 180.2) (CN); 218.0 (CO$_{eq}$); 233.7 (CO$_{ax}$); 271.5 (carbene C)
10	DMSO-*d*$_6$	0.82–0.90 (dd, 6H, Me$_2$); 1.74–2.04 (m, 2H, C*H*$_2$CHMe$_2$); 1.44–1.54 (13H, CH$_2$C*H*Me$_2$ + Me + CMe$_3$); 9.36 (s, 1H, NH)	22.8 (Me); 23.4 (Me); 23.8 (CH); 24.3 (C(*C*H$_3$)(^{t}Bu)); 27.6 (C(*C*H$_3$)$_2$); 44.8 (CH$_2$); 55.4 (*C*Me$_3$); 99.0 (*C*(^{t}Bu)(Me)); 180.6 (CN); 218.0 (CO$_{eq}$); 223.7 (CO$_{ax}$)
11	DMSO-*d*$_6$	0.94 (s, 9H, C(Me)$_3$); 1.50 (s, br, 12H, Me + C(Me)$_3$); 8.75 (s, 1H, NH)	17.5 (Me); 24.2 (C(*C*H$_3$)$_2$); 37.0 (*C*(Me)$_3$); 27.8 (C(*C*H$_3$)$_2$); 56.1 (*C*Me$_3$); 95.9 (*C*(^{t}Bu)(Me)); 179.9 (CN); 218.1 (CO$_{eq}$); 223.7 (CO$_{ax}$); 271.5 (carbene C)
12	DMSO-*d*$_6$	0.52 (d, 3H, Me); 1.16 (d, 3H, Me); 1.48 (s, 9H, C(Me)$_3$); 2.30 (m, 1H, C*H*(Me)$_2$); 5.12 (d, 1H, C*H*(^{i}Pr)); 9.68 (s, 1H, NH)	13.1 (Me); 19.5 (Me); 27.7 (C(*C*H$_3$)$_2$); 31.1 (CH); 55.0 (*C*Me$_3$); 88.6 (*C*(^{i}Pr)); 178.1 (CN); 218.1 (CO$_{eq}$); 223.6 (CO$_{ax}$); 272.9 (carbene C)
13		not measured	not measured
14	CD$_3$OD	1.56 (s, 9H, CMe$_3$); 1.84–2.00 (m, 8H, ^{c}Pent);	26.2, 39.8, 99.1 (^{c}Pent); 28.5 (C(*C*H$_3$)$_3$); 56.6 (*C*Me$_3$); 181.1 (CN); 219.5 (CO$_{eq}$); 225.1 (CO$_{ax}$); 276.5 (carbene C)
15	DMSO-*d*$_6$	1.20–1.96 (m, 19H, CMe$_3$ + ^{c}Hex); 9.32 (s, 1H, NH)	21.9, 23.7, 27.8, 28.3, 55.3, 90.1 (CMe$_3$ + ^{c}Hex); 181.2 (CN); 218.2 (CO$_{eq}$); 223.9 (CO$_{ax}$); 271.0 (carbene C)
16	CDCl$_3$	1.14–2.42 (m, 21H, Cy + ^{c}Hex); 4.10, 6.00 (br, 0.5H (each), NH)	22.0, 24.4, 27.0, 32.3, 34.4, 42.0, 53.6, 89.7, (Cy + ^{c}Hex); 181.2 (CN); 218.0 (CO$_{eq}$); 224.3 (CO$_{ax}$); 281.1 (carbene C)
17	DMSO-*d*$_6$	1.48 (s, 6H, CMe$_2$); 3.08 (s, 3H, Me); 10.06 (br, 1H, NH)	24.4 (C(*C*H$_3$)$_2$); 30.8 (Me); 87.3 (C(*C*H$_3$)$_2$); 198.7 (CO$_{eq}$) [b]; 204.5 (CO$_{ax}$)
18	DMSO-*d*$_6$	1.44 (s, 6H, CMe$_2$); 1.48 (s, 9H, CMe$_3$); 9.60 (s, 1H, NH)	23.9 (C(*C*H$_3$)$_2$); 27.7 (C(*C*H$_3$)$_2$); 55.5 (*C*(Me)$_3$); 90.0 (C(*C*H$_3$)$_2$); 183.5 (CN); 198.4 (CO$_{eq}$); 204.5 (CO$_{ax}$)
19	CDCl$_3$	1.56 (s, 3H, Me); 2.06–2.32 (m, 2H, *C*H$_2$CH$_2$CO); 2.20 (s, 3H, COMe); 2.52 (m, 2H, CH$_2$*C*H$_2$CO); 3.22 (s, 3H, CNMe); 6.88 (br, 1H, NH)	not measured
20	DMSO-*d*$_6$	0.62 (t, 6H, Me$_2$); 1.36 (q, 4H, (CH$_2$)$_2$); 1.70–2.06 (m, 10H, C$_6$H$_{10}$); 3.96 (m, br, 1H, *ipso*-H(Cy)); 9.74 (d, 1H, NH)	6.6 (Me); 24.1 ((CH$_2$)$_2$); 24.7, 28.7, 31.3, 53.6 (Cy); 94.4 (*C*Et$_2$); 181.5 (CN); 198.4 (CO$_{eq}$); 204.3 (CO$_{ax}$); 250.9 (carbene C)
21	DMSO-d$_6$	1.26–2.04 (m, 19H, CMe$_3$ + ^{c}Hex); 9.48 (s, 1H, NH)	21.0, 21.9, 23.7, 28.1, 55.5, 89.8 (CMe$_3$ + ^{c}Hex); 185.5 (CN); 198.6 (CO$_{eq}$); 204.8 (CO$_{ax}$); 249.2 (carbene C)
22	DMSO-d$_6$	1.14–2.08 (m, 10H, C$_6$H$_{10}$); 3.12 (br, 1H, *ipso*-H(Cy) + C*H*Ph); 7.30–7.64 (m, 5H, Ph); 9.66 (s, Br, 1H, NH)	not measured
23	CDCl$_3$	1.48 (s, 6H, CMe$_2$); 1.56 (s, 9H, CMe$_3$); 5.52 (br, 1H, NH)	25.0 (C(*C*H$_3$)$_2$); 28.3 (C(*C*H$_3$)$_3$); 56.4 (*C*Me$_3$); 88.1 (*C*(CH$_3$)$_2$); 181.7 (CN); 207.0 (CO$_{eq}$); 214.3 (CO$_{ax}$); 272.8 (carbene C)

[a] Chemical shifts, δ, as ppm downfield from Me$_4$Si as internal standard. [b] $^1J[^{183}\mathrm{W}/^{13}\mathrm{C}(\mathrm{CO_{eq}})] = 125.8$ Hz.

For the 3CC products at chromium, an unequivocal assignment to the signals at ca. 270 ppm has become possible through a ^{13}C-labelling of the cyano carbon atom in the starting complex [Cr(CN)(CO)$_5$]$^-$. These resonances thus lie at a much lower field as compared with those of the quasi-aromatic 4CC heterocycles (δ ca. 185 ppm) and are only marginally 'higher' than the corresponding values in typical Fischer carbenes ($\delta \geq$ 300 ppm). In the tungsten complex **26**, a ^{183}W–^{13}C(carbene) coupling constant of 88 Hz has been determined [5]; the ^{1}J values for the ^{183}W–^{13}C(CO$_{eq}$) coupling in **26** and **17** (ca. 126 Hz) are within the usual range [18]. The C4 ring carbon atom which carries the exocyclic amino nitrogen appears at $\delta \sim 180$ ppm, i.e. at markedly lower fields than in the related 4-amino-imidazolin-2-ylidenes ($\delta \sim 140$ ppm) (Table 2).

The ^{1}H NMR signals at ≥ 9 ppm disappear on D$_2$O addition, thereby confirming their assignment to the NH protons. Broadening of the lines by proton-exchange processes makes it difficult to recognize vicinal ^{3}J(NH-CH) coupling. This problem was solved by using DMSO-d_6 in which the proton exchange is slowed down. In this way, reasonable J values (8 Hz) for the coupling of the proton residing on the exocyclic nitrogen with the vicinal (C)H of the cyclohexyl substituent have been obtained from the spectra of complexes **3** and **20** which allow for their structural assessment as regards the correct tautomeric form.

In complex **10**, the asymmetric ring carbon (C5) carrying the methyl and isobutyl group renders the methylene protons of the ^{i}Bu substituent diastereotopic, thereby producing a higher order signal pattern. In perfect agreement with a ^{1}H NMR simulation [19], the two non-equivalent ^{i}Bu methyl groups give rise to two narrow doublets at high field, while the AB part of the overall ABMX$_3$Y$_3$ system consists of eight lines resulting from the coupling of the two methylene protons with the tertiary CH; as suggested by the integrated intensities, the M part is hidden under the close singlets of the methyl and ^{t}Bu groups. It actually comes into view as a poorly resolved multiplet shifted by 1.1 ppm to higher field when the spectrum is recorded in benzene-d_6 which, through specific π-interactions, effects severe changes in the resonance frequencies. Similar observations were made in the ^{1}H NMR of complex **12**; unlike in **10**, however, the two doublets of the diastereotopic Pr-methyl groups, the X$_3$Y$_3$ part of an overall AMX$_3$Y$_3$ system, are widely separated due to the proximity of the centre of chirality (Table 2).

2.3. X-Ray structure of 9

Complex **9** is the second 3CC product whose structure has been determined by X-ray analysis (Fig. 1). The structure of the first one, **26**, has been dealt with briefly in a preliminary account [5]. The stereochemistries of both molecules are absolutely congruent, although **9** is even more ideally shaped as regards the planarity of the five-membered ring with a maximum atom deviation of only ±0.002 Å (**26**, ±0.028 Å), and the approximate identity of the four consecutive multiple bond lengths along the O–C–N–C(–N$_{exo}$) atomic chain of 1.337 ±0.020 Å (**26**, 1.340 ±0.030 Å). The remaining endocyclic C–O and C–C bonds complementing the oxazoline rings in both **9** and **26** are clearly single bonds (Table 3).

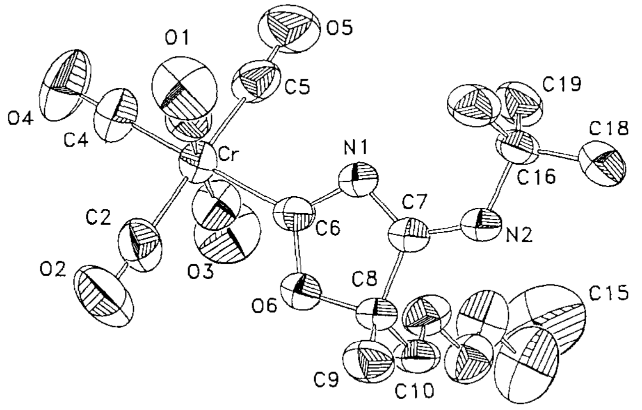
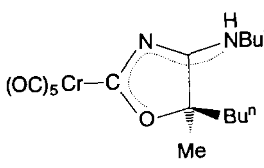
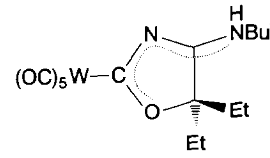


Fig. 1. ORTEP plot and labelling scheme for complex **9**. Thermal ellipsoids have been drawn to include 50% probability.



9



26

Major differences are encountered in the conformation of the heterocycles with respect to (i) the M(CO)$_5$ fragment and (ii) the planar 4-amino group. Thus, whilst in **9** a C6, N1, C7, C8, O6//C1, C3, C4, Cr interplanar angle of 62° has been calculated, the oxazoline ring and the *cis*-CO ligands are nicely staggered in **26**, as shown by a corresponding angle of 41.4°. More remarkably, with an interplanar angle of 64°, the heterocycle and its amine substituent in **9** are far from being coplanar, a conformation approximately adopted in **26**.

Compared with other bis(heteroatom)-stabilized carbene complexes, e.g. [Cr(CO)$_5${C(OEt)NMe$_2$}] (Cr–C$_{carbene}$ = 2.133(4) Å) [20], the chromium–carbene carbon distance in **9** is definitely at the short side as was the tungsten–carbene carbon distance (W–C$_{carbene}$ = 2.162(6) Å) in **26**. Together with the positions at very low fields of the ^{13}C NMR carbene signals (cf. Section 2.2) and the sequence of like C–O and C–N bond lengths symbolized by the dashed curve, this points to a special bonding situation as yet unprecedented by N,O-carbene ligands and complexes, respectively.

2.4. X-ray structure of a 4CC product (27)

An ORTEP drawing of the molecule of **27** [6] is shown in Fig. 2, the pertinent bond lengths and angles being given in Table 4. Unfortunately, a more profound discussion of the structural details and their electronic background is precluded by the large standard deviations; note, however, that the bonding parameters of **27** compare favourably with those of the molybdenum complex **28**, the first example of a 4CC product examined by X-ray methods, in the formation of which a phenylhydrazone had been incorporated in place of the primary amine [6]. Also note that the chromium–carbene carbon bond in **27** measuring 2.10(1) Å is significantly longer than that in the 3CC product **9** (cf. Section 3) which lies outside the range of values usually found for bis(heteroatom)-stabilized carbene–chromium species [21].

Table 3
Selected bond distances (Å), bond and interplanar angles (°) of complex **9** [a,b]

Bond distances			
Cr–C1	1.875(5)	Cr–C2	1.870(5)
Cr–C3	1.865(5)	Cr–C4	1.850(4)
Cr–C5	1.867(5)	Cr–C6	2.043(3)
C1–O1	1.149(6)	C2–O2	1.147(6)
C3–O3	1.154(6)	C4–O4	1.155(5)
C5–O5	1.155(5)		
C6–N1	1.354(4)	C7–N2	1.316(4)
C6–O6	1.359(4)	C7–C8	1.502(5)
N1–C7	1.337(4)	N2–C16	1.500(5)
O6–C8	1.462(4)	N2–H2	0.97(3)
C16–C17	1.521(7)	C10–C11	1.514(7)
C16–C18	1.517(6)	C11–C12	1.523(8)
C16–C19	1.521(7)	C12–C13	1.479(9)
C8–C9	1.533(7)	C13–C14	1.526(11)
C8–C10	1.508(6)	C14–C15	1.52(2)
Bond angles			
C1–Cr–C3	174.9(2)		
C2–Cr–C5	177.3(2)		
C4–Cr–C6	178.4(2)		
Cr–Cl–O1	176.8(4)	Cr–C2–O2	178.4(4)
Cr–C3–O3	178.3(4)	Cr–C4–O4	179.2(5)
Cr–C5–O5	176.9(4)		
N1–Cr–O6	111.4(3)	C6–O6–C8	110.0(3)
C6–N1–C7	107.6(3)	O6–C8–C7	99.0(3)
N1–C7–C8	112.0(3)		
N1–C7–N2	125.8(3)	Cr–C6–N1	126.9(3)
O6–C8–C9	108.2(3)	Cr–C6–O6	121.7(2)
N2–C7–C8	122.2(3)	C7–N2–H2	116.0(2)
O6–C8–C10	109.9(3)	C7–C2–C16	124.8(3)
C7–C8–C10	113.8(3)	N2–C16–C17	109.2(3)
C16–N2–H2	119.0(2)	C17–C16–C19	112.3(4)
N2–C16–C18	105.6(3)	C17–C16–C18	109.8(4)
N2–C16–C19	109.6(3)	C18–C16–C19	110.1(4)
C7–C8–C9	112.0(3)	C11–C12–C13	115.4(5)
C9–C8–C10	112.9(3)	C12–C13–C14	112.4(6)
C8–C10–C11	116.5(4)	C13–C14–C15	110.4(8)
C10–C11–C12	112.9(4)		
Best planes			
I: C6, O6, C8, C7, N1	II: N2, H2 C16	III: C2, C3, C5, C1, Cr	IV: C1, C3, C4, Cr
Interplanar angles			
I–II: 64.8(3)	I–III: 89.7(1)	II–III: 25.5(3)	
I–IV: 62(1)	II–IV: 76.3(3)	III–IV: 89.2(2)	

[a] E.s.d.s are given in parentheses, see Fig. 1 for atomic numbering.
[b] The labelling of the hydrogen atom follows that of the carbon atom to which it is attached.

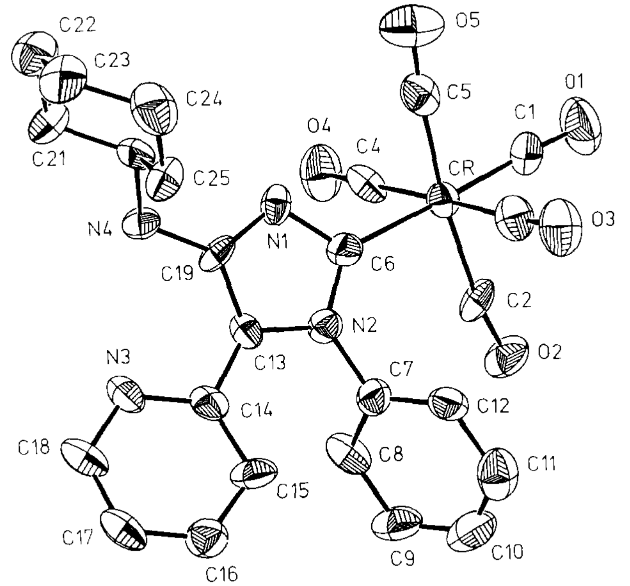
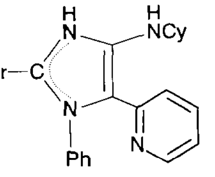
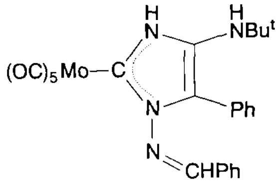


Fig. 2. ORTEP representation the structure of complex **27**. Hydrogen atoms have been omitted for clarity.



27



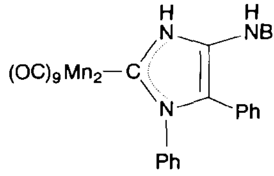
28

Complex **27** represents a sterically overcrowded imidazole derivative, with the consequence that neither the phenyl nor the 2-pyridyl ring is coplanar with the imidazole ring. Interplanar angles of 69.1° and 67.2°, respectively, are indicative of the severe repulsion of the *ortho*-hydrogen atoms that exists in the untwisted structure.

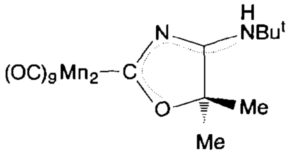
Within the five-membered heterocycle, despite its aromaticity, there is no uniformity of bond distance nor is there any sequence of like bond lengths as in the structures of the 3CC products **9** and **26** (cf. Section 2.3). Even if it is not as striking as in the case of $[\mathrm{Pd}\{\overline{\mathrm{CN(H)C(H)}{=}\mathrm{C(H)N}}\mathrm{Me}\}_4]\mathrm{I}_2$ or $\mathrm{NEt_3H}$-$[\mathrm{W}\{\overline{\mathrm{CN(H)C(CO_2Et)C(O^-)N}}\mathrm{Ph}\}(\mathrm{CO})_5]$ [22,23], the tendency towards a break-up of the 6π-electron system into two only loosely connected π-sections, the MC(N)N-carbene moiety and the transannular CC double bond, comes out clearly in the bonding parameters (Table 4). As these structural distortions must be parallelled by at least some loss of aromaticity, we have searched for and recently found chemical evidence for an 'activation by metallation' of the heterocycle in the extraordinary course of its oxidative removal from the metal (cf. Section 2.6).

2.5. *Three- and four-component condensations with cyanomanganese, -iron, -ruthenium and -cobalt complexes*

The reaction of the dinuclear cyanomanganese complex $NEt_4[Mn_2(CN)(CO)_9]$ with stoichiometric amounts of t-butyl isocyanide, benzaldehyde and aniline hydrochloride in ice-cold methanol gave a yellow compound, **29**, which was far less stable than the related mononuclear pentacarbonyl-chromium to -tungsten 4CC derivatives. Extensive decomposition took place in solution thereby affecting the NMR evidence. However, the presence in the mass spectrum of the molecular peak along with the required nine lines of CO fragmentation and the line for the 'metal-free' heterocycle is in full accord with the above formulation (see Table 5).



29



30

A 3CC product, **30**, could also be obtained from $[Mn_2(CN)(CO)_9]^-$ in 45% yield, the mass spectrum of which corresponds to that of **29** with additional lines for $[Mn_2]^+$, $[MnL]^+$ and $[MnCNH]^+$. Both dimanganese complexes show ν(NH) bands of medium intensity while only **30** exhibits the strong absorption at ca. 1600 cm^{-1} typical for the $N\overset{..}{-}C\overset{..}{-}O$ moiety present in the 3CC products.

The question arises whether the carbene ligand resides in an equatorial or an axial position in the Mn_2L_{10} coordination geometry. For axially substituted $Mn_2(CO)_9L$ complexes having an ideal C_{4v} symmetry, five infrared-active ν(CO) bands ($3A_1 + 2E$) are expected and have actually been observed for $[M_2(CN)(CO)_9]^-$ (M = Mn, Re) [24], while an equatorial L, i.e., L in a *cis* position relative to the metal–metal bond (C_s), should give rise to nine ($6A' + 3A''$). As diverse electrophilic reactions carried out by Behrens et al. with the coordinated cyanide of $[Mn_2(CN)(CO)_9]^-$ occurred with retention of configuration [25], it was plausible to expect the same for our multicomponent reactions. In fact, the IR spectrum in CH_2Cl_2 solution of **30** shows the required number of five ν(CO) absorptions.

Table 4
Selected bond distances (Å) and bond angles (°) of complex **27** [a,b]

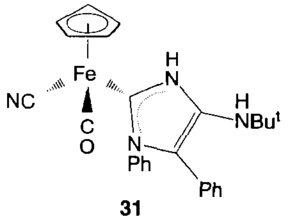
Bond distances			
Cr–C1	1.86(2)	Cr–C2	1.90(1)
Cr–C3	1.89(1)	Cr–C4	1.87(1)
Cr–C5	1.87(1)	Cr–C6	2.10(1)
C1–O1	1.14(1)	C2–O2	1.16(2)
C3–O3	1.16(2)	C4–O4	1.18(2)
C5–O5	1.17(2)		
C6–N1	1.38(2)	C6–N2	1.36(2)
C19–N1	1.40(2)	C13–C19	1.35(2)
C13–N2	1.43(1)	C7–C8	1.35(2)
C19–N4	1.38(2)	C7–C12	1.40(2)
C8–C9	1.39(2)	C9–C10	1.39(2)
C10–C11	1.38(2)	C11–C12	1.41(2)
C13–C14	1.46(2)	C14–C15	1.39(2)
C14–N3	1.37(2)	C18–N3	1.34(2)
C15–C16	1.40(2)	C16–C17	1.36(2)
C17–C18	1.37(3)		
C20–N4	1.50(1)	C20–C21	1.49(2)
C20–C25	1.50(2)	C21–C22	1.52(2)
C22–C23	1.51(2)	C23–C24	1.54(2)
C24–C25	1.54(2)		
N1–H1	1.01(1)	N4–H4	1.02(1)
Bond angles			
C1–Cr–C6	177.3(7)	C2–Cr–C5	173.1(6)
C3–Cr–C4	176.0(6)		
Cr–C1–O1	176(1)	Cr–C2–O2	172(1)
Cr–C3–O3	177(1)	Cr–C4–O4	177(1)
Cr–C5–O5	176(1)		
Cr–C6–N1	124(1)	Cr–C6–N2	133.4(9)
N1–C6–N2	103(1)	C8–C7–C12	123(1)
C8–C7–N2	122(1)	C12–C7–N2	115(1)
C7–C8–C9	120(1)	C8–C9–C10	118(1)
C9–C10–C11	122(2)	C10–C11–C12	119(1)
C7–C12–C11	117(1)	C14–C13–C19	128(1)
C14–C13–N2	127(1)	C19–C13–N2	104(1)
C13–C14–C15	125(1)	C13–C14–N3	112(1)
C15–C14–N3	123(1)	C14–C15–C16	117(1)
C15–C16–C17	120(2)	C16–C17–C18	120(2)
C17–C18–N3	123(1)	C13–C19–N1	108(1)
C13–C19–N4	131(1)	N1–C19–N4	121(1)
C21–C20–C25	111(1)	C21–C20–N4	108.8(9)
C25–C20–N4	112(1)	C20–C21–C22	113(1)
C21–C22–C23	110(1)	C22–C23–C24	111(1)
C23–C24–C25	110(1)	C20–C25–C24	111(1)
C6–N2–C7	124(1)	C6–N1–C19	112(1)
C6–N2–C13	113(1)	C7–N2–C13	123(1)
C14–N3–C18	117(1)	C19–N4–C20	120.5(9)
Best planes			
I: N1, C6, N2, C13, C19	II: C7, C8, C9, C10, C11, C12	III: C14, C15 C16, C17, C18, N3	
Interplanar angles			
I–II: 69.1(5)	I–III: 20.9(5)	II–III: 67.2(5)	

[a] E.s.d.s. are given in parentheses, see Fig. 2 for atomic numbering.
[b] The labelling of the hydrogen atoms follows that of the carbon atoms to which they are attached.

From the standpoint of an inorganic or organometallic chemist (which we take), an extensive variation of the cyano complex component appears particularly desirable for two reasons: Firstly, because in this way we can prove the general validity of our novel multicomponent cycloadditions with cyano complexes, and secondly, because valuable information might be obtained for the intended catalytic conductance of these reactions.

By choosing carbonyl(dicyano)cyclopentadienylferrate as the cyano complex component, we have, for the first time, *two* cyano ligands per metal atom available for cycloadditions. However, with t-butyl isocyanide, benzaldehyde and anilinium chloride, only one cyano group could be brought to reaction. After chromatographic work-up, the neutral complex **31** containing a chiral iron centre was isolated. The remaining unreacted CN ligand is clearly recognized by an IR band at 2081 cm^{-1}. The carbene resonance in the ^{13}C NMR appears at an exceptionally high field compared with other electron-rich carbene moieties, e.g. in [Fe(CN)-Cp(CO){C(NHMe)$_2$}] with δ(C$_{carbene}$) 214.4 ppm. In contrast, δ(CO) in **31** is very little changed from the value of the starting complex (δ 219.2 ppm [26]). According to the mass spectrum, CO, CN, Cp and ^{56}Fe are cleaved off, one after the other, from the highest ion [M]$^+$, leaving an intense peak which is that of the heterocycle.

A twofold 4CC of [Fe(CN)$_2$Cp(CO)]$^-$ has been achieved by reaction with double the molar amount of isobutyraldehyde, t-butyl isocyanide and ammonium hexafluorophosphate. The resulting pale yellow powdery product was quite air-sensitive. Complex **32** has been obtained only in a moderate yield and was immediately confirmed by the highest mass in the pos-FAB which was that of the complex cation.



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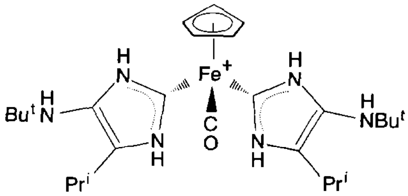


32

When applied to [Fe(CN)$_2$Cp(CO)]$^-$, the generally more strongly favoured 3CC gives the bis(carbene) species **33** exclusively [5]. Here, as in the case of [Fe(CN)Cp(dppe)], the order of addition of the components is crucial. In order to dissolve them in acetone, both cyano complexes were first protonated with HBF$_4$ before the isocyanide was added. Contrary to reports in the literature, there was no evidence for the forma-

Table 5

Mass spectroscopic data for the complexes **1–23**: (EI (80 eV)) [m/z (rel. intensity)] [a]

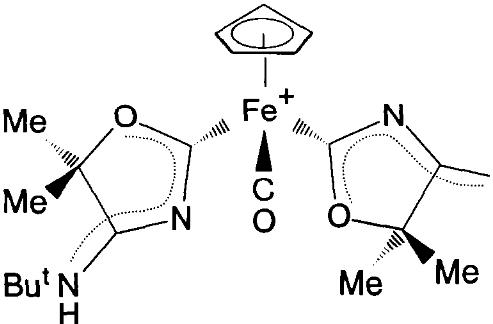
Complex	[M(CO)$_5$L]$^+$	[M(CO)$_4$L]$^+$	[M(CO)$_3$L]$^+$	[M(CO)$_2$L]$^+$	[M(CO)L]$^+$	[ML]$^+$	[MCNH]$^+$	[M]$^+$
1	318 (14)	290 (2)	262 (3)	234 (8)	206 (23)	178 (100)		52 (22)
2	360 (14)		304 (3)	276 (6)	248 (18)	220 (100)	79 (7)	52 (11)
3	386 (11)		330 (2)	302 (5)	274 (26)	246 (100)	79 (17)	52 (24)
4	390 (10)		334 (1)	306 (3)	278 (23)	250 (100)	79 (10)	52 (47)
5	394 (11)	360 (1)	338 (6)	310 (7)	282 (21)	254 (100)		52 (61)
6	472 (16)			388 (7)	360 (37)	332 (100)	79 (5)	52 (28)
7	374 (13)		318 (2)	290 (3)	262 (18)	234 (100)	79 (5)	52 (8)
8	402 (10)		346 (1)	318 (2)	290 (16)	262 (100)	79 (5)	52 (9)
9	430 (7)			346 (2)	318 (8)	290 (100)	79 (4)	52 (7)
10	402 (8)			318 (2)	290 (16)	262 (100)	79 (6)	52 (12)
11	402 (12)		346 (2)	318 (3)	290 (17)	262 (100)	79 (5)	52 (11)
12	374 (7)			290 (3)	262 (14)	234 (100)	79 (32)	52 (41)
13	468 (13)		412 (3)		356 (17)	328 (100)	79 (58)	52 (39)
14	386 (11)		330 (2)	302 (4)	274 (18)	246 (100)	79 (12)	52 (23)
15	400 (8)		344 (2)	316 (2)	288 (18)	260 (100)	79 (12)	52 (15)
16	426 (14)		370 (2)	342 (5)	314 (35)	286 (100)	79 (6)	52 (12)
17	450 (38)	422 (28)			338 (16)	310 (19)		
18	492 (13)	464 (5)		408 (7)	380 (4)	353 (29)		
19	506 (15)		450 (14)	422 (7)		366 (8)		
20	546 (43)	518 (24)		462 (21)	434 (24)	404 (52)		
21	532 (5)	504 (1)		448 (19)		392 (13)		
22	566 (6)			482 (7)				
23	406 (6)			322 (7)	294 (10)	266 (10)		98 (8)

[a] L = 4-amino oxazolin-2-ylidene.

tion of the stable *B*-isocyanide complex [Fe(CNBF$_3$)-Cp(dppe)] [27,28]. Both salt-like products (**33**, **34**) have been purified by column chromatography using polar solvents such as methanol and identified primarily by the pos-FAB peaks of their complex cations.

The ruthenium analogue of [Fe(CN)Cp(dppe)], i.e. [Ru(CN)Cp(dppe)], underwent a particularly smooth 3CC to give **35** in a high yield. This was not unexpected as [Ru(CN)Cp(PPh$_3$)$_2$] had earlier turned out to be an ideal starting material for all kinds of electrophilic additions to the coordinated cyanide [29].

In order to establish the generality of the 3CC and 4CC reactions of cyano complexes, the dicyanocobaloxime N^{n}Bu$_4$[Co(CN)$_2$(dmgH)$_2$] has been tested as a typically 'non-organometallic' cyano complex component. After mixing stoichiometric amounts of the respective reagents, neutral mono-3CC (**36**) and -4CC products (**37**–**39**) were isolated. In each complex, the remaining cyano ligand was clearly identified by an IR band at ca. 2140 cm^{-1}. Again we tried to react both cyano ligands in [Co(CN)$_2$(dmgH)$_2$]$^-$ by applying a twofold molecular amount of benzaldehyde, cyclohexyl isocyanide and anilinium chloride. However, the spectra (IR, NMR) and elemental analyses of the resulting product (**40**) were in favour of just another monocarbene complex, although its low solubility in less polar media and its greenish colour seemed to contradict this interpretation. The problem was solved by mass spectroscopy, in the pos-FAB of which the [Co-(dmgH)$_2$L$_2$]$^+$ cation (L = 4-aminoimidazolin-2-ylidene), i.e. the anticipated product of a twofold 4CC, was actually the highest intensity line; the simultaneous presence of an unchanged [Co(CN)$_2$(dmgH)$_2$]$^-$ anion followed from its mass line in the neg-FAB spectrum of **40**. Obviously, the salt-like product rapidly precipitates from the reaction mixture, thereby precluding any further transformation of the anionic dicyano complex.



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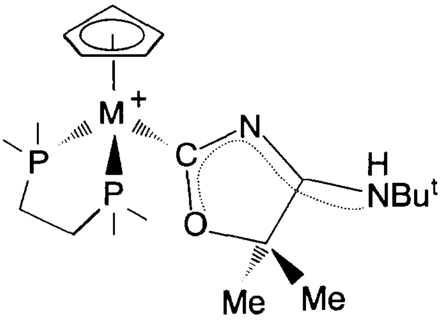
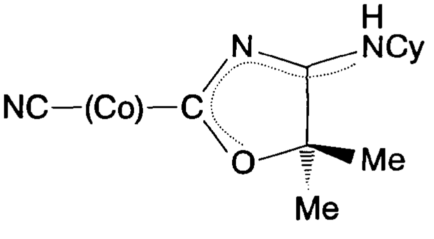


(M= Fe(**34**), Ru(**35**))



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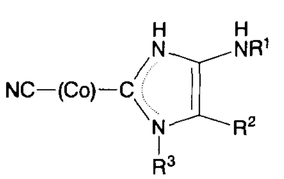
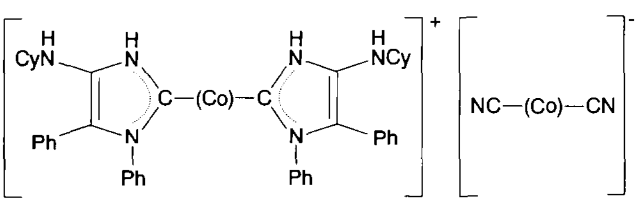


	37	**38**	**39**
R¹	Cy	Cy	Bu^t
R²	Ph	Tol^p	Tol^p
R³	Ph	Ph	Ph

[(Co)= Bis(dimethylglyoximato)cobalt]



40

2.6. Detachment of the heterocyclic ligand from the complex

There are several methods of cleaving the carbene ligand off the metal, the ones most frequently used being thermolysis [30] or oxidative degradation of the complex. In the latter reaction, which is usually carried out under phase-transfer conditions with a large excess of KMnO$_4$ in the presence of Fe^{3+} [3] or, cleaner, with

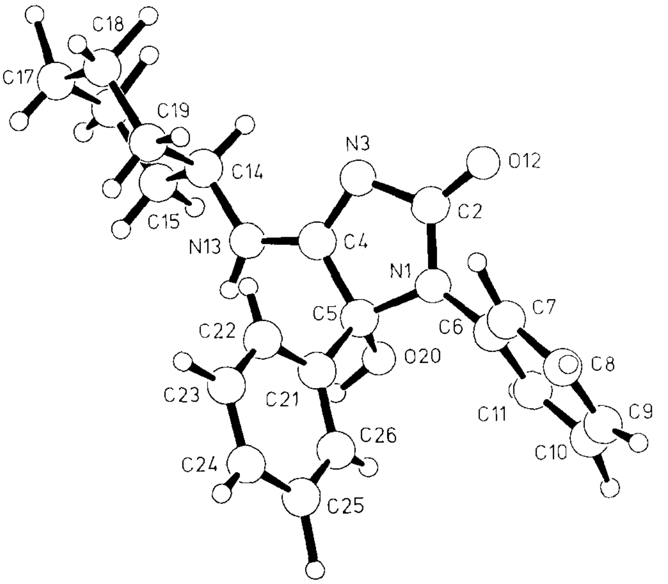
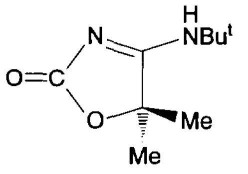


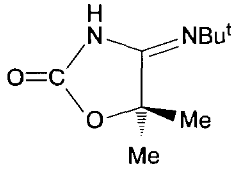
Fig. 3. Structure of complex **48**. Selected bond distances (Å): N1–C2, 1.361(4); C2–N3, 1.400(4); N3–C4, 1.315(4); C4–C5, 1.520(4); C5–N1, 1.462(4); C5–O20, 1.407(4); C2–O12, 1.224(4).

Ce^{4+}, the metal ends up in a higher oxidation state depleted of its ligand sphere while the carbene carbon is converted into a carbonyl group.

Oxidative cleavage with $KMnO_4/Fe^{3+}$ in acetone/water of the 3CC product **2** gave high yields of the respective oxazolinone which exists in one of the two tautomeric forms, **A** or **B** [5]. The two-step synthetic approach via transition metal complexes to this class of biologically and pharmaceutically active substances is thus clearly superior to the purely organic procedure requiring four steps [31].



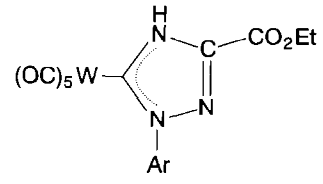
A



B

However, when applied to the tungsten-bonded carbenoid triazole **41**, the product of a [3 + 2] cycloaddition between a tungstenio nitrile ylid, $[W(CO)_5\{C^+{=}N{-}C^-H{-}CO_2Et\}]^-$, and an aryldiazonium species, oxidation with the same reagent obviously affected only the metal which subsequently released the N4–*H* to C5–*H* tautomerized 1-aryl-3-carbethoxy-1,2,4-triazole(**42**) [32]. Substitution with retention of the oxidation state of *both* the metal complex fragment *and* the heterocycle was of particular interest to us for the intended catalytic performance of the above 3CC and 4CC reactions. Displacement of aminocarbene ligands from complexes of the type $[Cr(CO)_5\{C(R)NHR'\}]$ had been achieved earlier with pyridine [33]. In accordance with this, action on a 4CC complex, **43**, of an excess of pyridine in boiling n-hexane led to the C2-*H*-4-aminoimidazole **44**, the structure of which was assessed by X-ray analysis [6,34].

In contrast to 4-amino-oxazolin-2-ones or 4-imino-oxazolidin-2-ones, respectively, the hydantoin-4-imides **45** are easily accessible by the direct organic 4CC route from KOCN, isocyanide, aldehyde and amine hydrochloride [1b]. As the same type of heterocycle was expected to result from oxidative degradation with $KMnO_4/Fe^{3+}$ of the 4-aminoimidazolin-2-ylidene complexes, the pursuit of this synthetic route appeared meaningless. Still, in order to complete our reactivity studies, the 4CC product complex **46** was subjected to this kind of oxidation. Very surprisingly, an organic product (**48**) carrying an additional *hydroxy* function in the 5-position was isolated in high yield. Verification of this result was achieved by an X-ray structure analysis of **48** (Fig. 3), details of which will be reported elsewhere [34]. The same is true for the structural investigation of a second member of the 4-amino-5-*hydroxy*-imidazol-2-one family, **49**, again prepared by oxidative decomposition with $KMnO_4/Fe^{3+}$ of the parent complex **47**.



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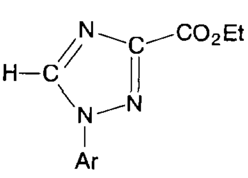

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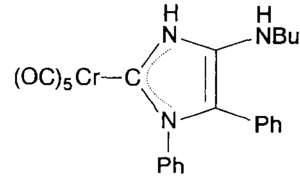

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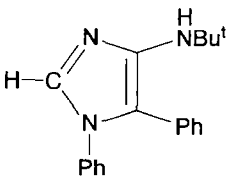

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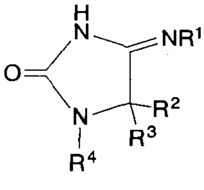
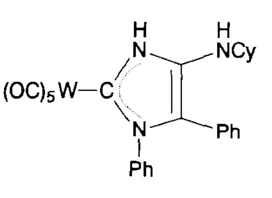


45



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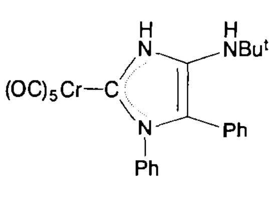

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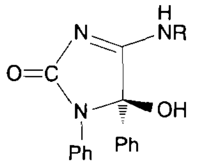

(R = Cy(**48**), Bu^t (**49**))

Nevertheless it appears desirable to mention some of the most interesting results: (i) In contrast to **48** which in the crystal lattice exists as a racemate, **49** crystallizes optically resolved as a conglomerate in the space group $P2_12_12_1$. The chiral resolution is considered to be a consequence of a very special type of crystal packing, viz. that of an orthogonally interconnected layer structure. (ii) Despite their non-aromaticity, the imidazole rings in **48** and **49** are planar as are all phenyl rings. None of the phenyl groups, however, is coplanar with its imidazole ring; their actually heavy twisting is regarded a molecular property caused by the steric overcrowding of these imidazole derivatives (cf. Section 2.4). (iii) All potential H-bond donors and acceptors are involved in the hydrogen-bonding scheme of **48**, while the crystal structure of **49** is determined by both extensive hydrogen bonding *and* intermolecular edge–plane π-interactions between the phenyl rings [34].

As the most plausible method of formation of the 4-amino-5-*hydroxy*imidazolin-2-ones **48** and **49**, we consider epoxidation of the double bond between C4 and C5, followed by a rearrangement which comprises ring-opening with concomitant (N3)H to O migration. Very remarkably, this is the first chemical evidence of what we call ‘activation of heterocycles by C-metallation’, a term which describes the structural distortions relative to the free aromatic systems of C2–metal-bonded carbenoid oxazoles and imidazoles (cf. Section 2.4).

In summary, the work accumulated so far on organometallic 3CC and 4CC reactions and products reflects the tremendous benefit organic synthesis obtains from the use of transition metals. Not only do they open up an extremely efficient and versatile access to heterocycles with interesting substitution patterns and promising biological activities, what is even more convincing, in the present case, is the various chances for novel derivatizations of heterocycles on removing the multifunctional metal substituent.

Further studies on the reactivity of C2–metal coordinated 4-amino-oxazolines and -imidazoles, with particular emphasis on new methods of ligand detachment, are in progress in our laboratory.

3. Experimental details

All operations were carried out in an inert gas atmosphere (Ar) using Schlenk tube techniques. The solvents were deoxygenated and dried prior to use. Infrared spectra were recorded on a Perkin-Elmer 983 IR spectrometer. C, H and N analyses were obtained with a Heraeus CHN-Rapid-Elementaranalysator. Melting points were taken on a Gallenkamp melting point apparatus and are uncorrected. FAB mass spectra were obtained with a CH5-DF Varian MAT (Bremen) instrument and EI mass spectra (80 eV) with a Varian MAT 711 (Bremen) instrument. Proton and ^{13}C NMR spectra were recorded on a Bruker AM 250 and 270 instrument. Silica gel (100–200 μm) from ICN was used for column chromatography. The cyano complexes $NEt_4[M(CN)(CO)_5]$ (M = Cr, Mo, W) [35] and $N^nBu_4[Co(CN)_2(dmgH)_2]$ [36] were prepared by published methods. All other reagents were purchased from Aldrich.

3.1. General procedure for the preparation of the pentacarbonyl{4-amino-Δ^3-oxazolin-2-ylidene}chromium, -molybdenum and -tungsten complexes 1–23

To a stirred solution consisting of 1.4 mmol of $NEt_4[M(CN)(CO)_5]$ (M = Cr, Wo, W) in 10 ml of the ketone was added at 0°C 1.4 mmol of HBF_4 (etheral solution, 54%), followed by a dropwise addition of 1.4 mmol of the isocyanide in 5 ml of the ketone. The mixture was then allowed to warm to room temperature overnight. Silica gel was added and the mixture evaporated to dryness. The resulting powder was transferred to a chromatography column charged with silica gel (2 × 20 cm) and eluted first with petroleum ether/diethyl ether (1 : 1) and then with pure diethyl ether. The light yellow fractions were collected, evaporated to dryness and recrystallized from dichloromethane/petroleum ether (1 : 1), resulting in a yellow powder.

For the preparation of complex **13**, 0.48 g (1.4 mmol) of $NEt_4[Cr(CN)(CO)_5]$ were dissolved in 10 ml of dichloromethane, mixed with 1.6 mmol of hexafluoroacetone sesquihydrate and then 0.21 ml (1.4 mmol) of HBF_4 (etheral solution, 54%) and 0.15 ml (1.4 mmol) of t-butyl isocyanide in 5 ml of dichloromethane were

Table 6
Analytical and other data

Complex	Molecular weight (g mol^{-1})	Melting point (dec.) (°C)	Yield (%)	Analyses (%)			
					C	H	N
1	$C_{11}H_{10}CrN_2O_6$	145	77	(Calc.)	41.52	3.14	8.80
	(318.23)			(Found)	41.50	3.34	8.65
2	$C_{14}H_{16}CrN_2O_6$	140	79	(Calc.)	46.6	4.44	7.77
	(360.32)			(Found)	46.57	4.60	7.68
3	$C_{16}H_{18}CrN_2O_6$	130	81	(Calc.)	49.74	4.66	7.25
	(386.36)			(Found)	49.83	4.97	7.13
4	$C_{14}H_{14}CrN_2O_8$	139	56	(Calc.)	43.07	3.59	7.18
	(390.30)			(Found)	42.97	4.01	6.71
5	$C_{17}H_{14}CrN_2O_6$	100	49	(Calc.)	51.78	3.55	7.11
	(394.33)			(Found)	51.73	3.68	6.97
6	$C_{18}H_{16}CrN_2O_8S$	130	53	(Calc.)	45.76	3.39	5.93
	(472.43)			(Found)	44.79	3.82	5.64
7	$C_{15}H_{18}CrN_2O_6$	140	75	(Calc.)	48.13	4.81	7.49
	(374.35)			(Found)	47.72	4.91	7.27
8	$C_{17}H_{22}CrN_2O_6$	110	77	(Calc.)	50.75	5.47	6.97
	(402.21)			(Found)	50.59	5.56	6.86
9	$C_{19}H_{26}CrN_2O_6$	115	67	(Calc.)	53.02	6.05	6.51
	(430.47)			(Found)	53.12	6.43	6.43
10	$C_{17}H_{22}CrN_2O_6$	115	78	(Calc.)	50.75	5.47	6.97
	(402.41)			(Found)	50.66	5.51	6.88
11	$C_{17}H_{22}CrN_2O_6$	138	70	(Calc.)	50.75	5.47	6.97
	(402.41)			(Found)	50.75	5.56	6.91
12	$C_{15}H_{18}CrN_2O_6$	128	33	(Calc.)	48.13	4.81	7.49
	(374.35)			(Found)	48.19	5.05	7.52
13	$C_{14}H_{10}CrF_6N_2O_6$	120	21	(Calc.)	35.89	2.14	5.90
	(468.26)			(Found)	37.21	2.88	6.32
14	$C_{16}H_{18}CrN_2O_6$	170	74	(Calc.)	49.74	4.66	7.25
	(386.36)			(Found)	49.50	4.92	6.90
15	$C_{17}H_{20}CrN_2O_6$	155	88	(Calc.)	51.04	5.04	7.00
	(400.07)			(Found)	52.19	5.41	6.85
16	$C_{15}H_{22}CrN_2O_6$	172	69	(Calc.)	53.52	5.20	6.60
	(426.43)			(Found)	53.57	5.30	6.45
17	$C_{11}H_{10}N_2O_6W$	135	72	(Calc.)	29.33	2.22	6.22
	(450.08)			(Found)	29.33	2.57	6.57
18	$C_{14}H_{16}N_2O_6W$	130	65	(Calc.)	34.15	3.25	5.69
	(492.17)			(Found)	34.07	3.33	5.67
19	$C_{14}H_{14}N_2O_7W$	200	41	(Calc.)	33.22	2.79	5.53
	(506.15)			(Found)	33.53	2.99	5.55
20	$C_{18}H_{22}N_2O_6W$	120	61	(Calc.)	39.56	4.03	5.13
	(546.27)			(Found)	39.84	4.21	4.82
21	$C_{17}H_{20}N_2O_6W$	135	43	(Calc.)	38.39	3.74	5.27
	(532.08)			(Found)	40.72	4.48	5.21
22	$C_{20}H_{18}N_2O_6W_2$	133	48	(Calc.)	42.43	3.20	4.95
	(566.25)			(Found)	43.12	3.51	4.91
23	$C_{14}H_{16}MoN_2O_6$	130	66	(Calc.)	41.58	3.96	6.93
	(404.26)			(Found)	41.52	4.01	6.82
29	$C_{28}H_{21}Mn_2N_3O_9$	75	20	(Calc.)	51.45	3.21	6.42
	(653.40)			(Found)	54.23	4.08	6.44
30	$C_{18}H_{16}Mn_2N_2O_{10}$	140	45	(Calc.)	40.75	3.02	5.28
	(530.88)			(Found)	39.96	3.22	5.29
31	$C_{26}H_{26}FeN_4O$	195	68	(Calc.)	66.95	5.58	12.02
	(466.41)			(Found)	63.56	5.67	11.18
32	$C_{26}H_{43}F_6FeN_6OP$	95	30	(Calc.)	47.56	6.55	12.80
	(656.11)			(Found)	49.49	6.67	12.25
34	$C_{40}H_{45}BF_4FeN_2OP_2$	175	54	(Calc.)	62.04	5.86	3.62
	(774.41)			(Found)	62.25	6.20	3.33
35	$C_{40}H_{45}BF_4N_2OP_2Ru$	170	80	(Calc.)	58.62	5.53	3.42
	(819.64)			(Found)	58.35	6.15	2.99
36	$C_{20}H_{32}CoN_7O_5$	180	37	(Calc.)	47.13	6.33	19.25
	(509.17)			(Found)	47.37	6.64	18.61

Table 6 (continued)

Complex	Molecular weight (g mol^{-1})	Melting point (dec.) (°C)	Yield (%)	Analyses (%)			
					C	H	N
37	$C_{30}H_{37}CoN_8O_4$	179	46	(Calc.)	56.96	5.89	17.71
	(632.56)			(Found)	54.74	5.59	16.84
38	$C_{31}H_{39}CoN_8O_4$	204	38	(Calc.)	57.67	5.93	17.35
	(646.58)			(Found)	56.15	6.23	16.88
39	$C_{29}H_{37}CoN_8O_4$	185	35	(Calc.)	56.13	6.00	18.05
	(646.58)			(Found)	55.96	6.04	16.35
40	$C_{60}H_{74}Co_2N_{16}O_8$	145	11	(Calc.)	56.96	5.89	17.71
	(1264.45)			(Found)	54.74	5.56	16.84
48	$C_{21}H_{23}N_3O_2$	200	83	(Calc.)	72.18	6.63	12.03
	(349.43)			(Found)	71.52	6.51	11.55
49	$C_{19}H_{21}N_3O_2$	195	82	(Calc.)	70.57	6.55	12.99
	(323.40)			(Found)	69.72	6.38	11.59

added at 0°C. Work-up of the reaction mixture as described for the general procedure resulted in **13** as a yellow powder.

For spectroscopic data see Tables 1–3, for elemental analyses and physical properties, see Table 6.

3.2. Preparation of 29

Stoichiometric amounts of benzaldehyde, t-butyl isocyanide and aniline hydrochloride were mixed with 0.50 g (0.97 mmol) of $NEt_4[Mn_2(CN)(CO)_9]$ in methanol at 0°C. The mixture was allowed to warm up to room temperature overnight. Chromatographic work-up on a column charged with silica gel (petroleum ether/diethyl ether (3 : 1)) resulted in a yellow powder of **29**. ^{1}H NMR($CDCl_3$) δ: 1.12 (s, 9H, Me); 6.90–7.44 (m, 10H, Ph); 9.3 (s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$) δ: 30.0 ($C(CH_3)_3$); 53.9 (CMe_3); 113.9–134.4 (Ph + C5); 138.7 (C4); 183.4 (carbene-C); 224.0 (CO). IR (KBr) (cm^{-1}): 3442 (m) (NH); 2079 (s), 2004 (s), 1960 (vs), 1927 (s), 1914 (s) (CO); 163 (m), 1597 (m) (heterocyle). MS (EI) *m/z* (rel. int. (%)): 653 (1) $[Mn_2(CO)_9L]^+$; 625 (1) $[Mn_2(CO)_8L]^+$; 541 (2) $[Mn_2(CO)_5L]^+$; 513 (4) $[Mn_2(CO)_4L]^+$; 485 (1) $[Mn_2(CO)_3L]^+$; 457 (9) $[Mn_2(CO)_2L]^+$; 401 (4) $[Mn_2L]^+$; 346 (66) $[MnL]^+$; 291 (26) $[L]^+$.

For elemental analyses and physical properties, see Table 6.

3.3. Preparation of nonacarbonyl{4-t-butylamino-5,5-dimethyl-Δ^3-oxazolin-2-ylidene}dimanganese (30)

Stoichiometric amounts of HBF_4 (etheral solution, 54%) and t-butyl isocyanide were mixed with 0.50 g (0.97 mmol) of $NEt_4[Mn_2(CN)(CO)_9]$ in acetone at 0°C. Work-up of the reaction mixture as described for the general procedure resulted in yellow crystals of **30**. ^{1}H NMR (DMSO-d_6) δ: 1.50 (s, br, 15H, $CMe_3 + CMe_2$) ppm. ^{13}C NMR (DMSO-d_6) δ: 23.3 ($C(CH_3)_2$); 27.2 ($C(CH_3)_3$); 54.8 (CMe_3); 88.0 (CMe_2); 179.4 (C4); 220.2, 221.4, 222.5 (CO). IR (KBr) (cm^{-1}): 3397 (m) (NH); 2083 (m), 2016 (s), 1982 (vs), 1953 (s), 1919 (s) (CO); 1607 (s) 1514 (w), 1502 (m) (heterocycle). MS (EI) *m/z* (rel. int. (%)): 530 (1) $[Mn_2(CO)_9L]^+$; 418 (2) $[Mn_2(CO)_5L]^+$; 390 (4) $[Mn_2(CO)_4L]^+$; 362 (2) $[Mn_2(CO)_3L]^+$; 335 (19) $[Mn_2(CO)_2L]^+$; 278 (12) $[Mn_2L]^+$; 223 (59) $[MnL]^+$; 110 (15) $[Mn_2]^+$; 82 (24) $[MnCNH]^+$; 55 (100) $[Mn]^+$.

3.4. Preparation of 31

$K[Fe(CN)_2Cp(CO)]$ (0.50 g, 2.08 mmol) was dissolved in 20 ml of absolute methanol at ice-bath temperature. To this solution was added 0.21 ml (2.08 mmol) of freshly distilled benzaldehyde, 0.24 ml (2.08 mmol) of t-butyl isocyanide and 0.27 g of aniline hydrochloride. The reaction mixture was stirred for several hours during which time it was allowed to warm to room temperature. The yellow precipitate was collected on a D_4 frit and washed with a small amount of petroleum ether. The solution was evaporated to dryness and the residue washed several times with ether. The combined solids were then recrystallized from diethyl ether/methanol to give 0.66 g (68%) of **31**. ^{1}H NMR ($CDCl_3$) δ: 1.18 (s, 9H, $C(Me)_3$); 3.28 (s, 1H, NH); 4.24 (s, 5H, Cp); 6.96–7.68 (m, 10H, Ph); 10.44 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ: 30.1 ($C(CH_3)_3$); 53.9 ($C(Me)_3$); 82.0 (Cp); 125.8–134.6 (Ph + C5); 139.7 (C4); 177.4 (carbene-C); 220.6 (CO). IR (KBr) (cm^{-1}): 3289 (w) 3210 (w) (NH); 2081 (s) (CN); 1941 (s) (CO); 1642 (w), 1595 (w) (heterocycle). MS (EI) *m/z* (rel. int. (%)): 466 (7) $[Fe(Cp)(CO)(CN)L]^+$; 438 (32) $[Fe(Cp)(CN)]^+$; 412 (26) $[Fe(Cp)]H^+$; 291 (93) $[L]^+$; 276 (96) $[L\text{-}Me]^+$; 235 (100) $[L\text{-}Me\text{-}C_3H_5]^+$.

For elemental analyses and physical properties, see Table 6.

3.5. Preparation of 32

To a solution of 0.50 g (2.08 mmol) of $K[Fe(CN)_2Cp(CO)]$ in 20 ml of methanol was added with stirring at 0°C 0.38 ml (4.17 mmol) of freshly distilled iso-butyraldehyde, 0.47 ml (4.17 mmol) of t-butyl isocyanide and 0.68 g (4.17 mmol) of ammonium hexafluorophosphate. Stirring was continued for 16 h at room temperature. Some silica gel was added and the solvent removed. The solid residue was then transferred to a chromatography column (2 × 15 cm) charged with silica gel and eluted with diethyl ether. The first light yellow fraction contained the product. After the solvent had been removed, an intensely yellow very air-sensitive solid (0.41 g, 30%) remained which was washed with petroleum ether and dried in vacuum. ^{1}H NMR (DMSO-d$_6$) δ: 0.78–1.52 (30H, C(Me)$_3$, CH(M^e)$_2$); 2.92 (m, 2H, C*H*(Me)$_2$); 3.72 (s, 2H, NH); 4.76 (s br, 5H, Cp); 10.54 (br, 2H, NH); 10.94 (br, 2H, NH). ^{13}C NMR (DMSO-*d*$_6$) δ: 20.8 (CH(*C*H$_3$)$_2$); 21.8 (*C*HMe$_2$); 28.4 (C(*C*H$_3$)$_3$); 51.4 (*C*(Me)$_3$); 82.3 (Cp); 129.5 (C5); 129.6 (C4); 173.1 (carbene-C); 220.5 (CO). IR (KBr) (cm^{-1}): 3422 (m); 3252 (m) (NH); 1931 (vs) (CO); 1667 (m), 1652 (m) (heterocycle); 847 (s), 557 (s) (PF$_6^-$). MS (pos-FAB) *m/z* (rel. int. (%)): 511 (12) [Fe(Cp)(CO)(L)$_2$]$^+$; 483 (5) [Fe(Cp)(L)$_2$]$^+$; 418 (4) [Fe(L)$_2$]$^+$.

For elemental analyses and physical properties, see Table 6.

3.6. *Preparation of (4-t-butylamino-5,5-dimethyl-Δ^3-oxazolin-2-ylidene)(η-cyclopentadienyl){bis(diphenylphosphino)ethane}iron tetrafluoroborate* (**34**)

To a stirred suspension of 0.5 g (0.9 mmol) of [Fe(CN)Cp(dppe)] in 20 ml of acetone was added 0.14 ml (0.9 mmol) of HBF$_4$ (etheral solution, 54%) at 0°C, followed by a dropwise addition of 0.1 ml (0.9 mmol) of t-butyl isocyanide. The brown solution was then allowed to warm to room temperature overnight. Silica gel was added and the mixture evaporated to dryness. The resulting powder was transferred to a chromatography column charged with silica gel (2 × 20 cm) and eluted first with dichloromethane and then with dichloromethane/methanol (5 : 1). The yellow to brown fractions were collected, evaporated to dryness and recrystallized from dichloromethane/diethyl ether, resulting in a yellow powder. ^{1}H NMR (CDCl$_3$) δ: 0.82 (s, 6H, CMe$_2$); 1.08 (s, 9H, CMe$_3$); 1.82 (s, br, 1H, NH); 2.85–3.20 (m, 4H, CH$_2$CH$_2$); 4.38 (s, 5H, Cp); 7.10–7.64 (m, 20H, Ph). ^{13}C NMR (CDCl$_3$) δ: 22.6 (C(*C*H$_3$)$_2$); 27.7 (C(*C*H$_3$)$_3$); 29.9 ('vt', dppe); 54.2 (*C*Me$_3$); 84.6 (Cp); 88.2 (*C*Me$_2$); 128.2–132.6 (Ph); 177.9 (carbene-C). IR (KBr) (cm^{-1}): 3310 (m) (NH); 1607 (st), 1571 (s), 1533 (m) (heterocycle). MS (pos-FAB) *m/z* (rel. int. (%)): 687 (100) [FeCp(dppe)L]$^+$; 519 (32) [FeCp(dppe)]$^+$; 148 (71) [FeCp(CNH)]$^+$; 121 (61) [FeCp]$^+$.

For elemental analyses and physical properties, see Table 6.

3.7. *Preparation of (4-t-butylamino-5,5-dimethyl-Δ^3-oxazolin-2-ylidene)(η-cyclopentadienyl){bis(diphenylphosphino)ethane}ruthenium tetrafluoroborate* (**35**)

To a stirred suspension of 0.59 g (1.0 mmol) of [Ru(CN)Cp(dppe)] in 20 ml of acetone was added 0.15 ml (1.0 mmol) of HBF$_4$ (etheral solution, 54%) at 0°C, followed by dropwise addition of 0.11 ml (1.0 mmol) of t-butyl isocyanide. The yellow solution was then allowed to warm up to room temperature overnight. Silica gel was added and the mixture evaporated to dryness. The resulting powder was transferred to a chromatography column charged with silica gel (2 × 20 cm) and eluted with dichloromethane/methanol (20 : 1). The yellow fraction was evaporated to dryness and recrystallized from dichloromethane/diethyl ether, resulting in a yellow powder. ^{1}H NMR (CDCl$_3$) δ: 0.9 (s, 6H, CMe$_2$); 1.10 (s, 9H, CMe$_3$); 1.80 (s, br, 1H, NH); 2.80–8.15 (m, 4H, CH$_2$CH$_2$); 4.90 (s, 5H, Cp); 7.10–7.70 (m, 20H, Ph) ppm. ^{13}C NMR (CDCl$_3$)δ: 17.8–33.4 (aliphatic-C); 54.6 (*C*Me$_3$); 80.6 (Cp); 88.0 (*C*Me$_2$); 124.2–133.6 (Ph); 180.0 (carbene-C). IR (KBr) (cm^{-1}): 3307 (s) (NH); 1680 (s) (heterocycle). MS (pos-FAB) *m/z* (rel. int. (%)): 733 (100) [RuCp(dppe)L]$^+$; 565 (30) [RuCp(dppe)]$^+$.

For elemental analyses and physical properties, see Table 6.

3.8. *Preparation of* **36**

To a stirred solution of 1.0 g (1.7 mmol) of N^{n}Bu$_4$-[Co(CN)$_2$(dmgH)$_2$] in 50 ml of acetone was added 0.23 ml (1.7 mmol) of HBF$_4$ (etheral solution, 54%) at 0°C, followed by dropwise addition of 0.20 ml (1.7 mmol) of cyclohexyl isocyanide. After 12 h, the mixture was concentrated and transferred to a chromatography column charged with silica gel (2 × 25 cm) and eluted with dichloromethane/acetone (1 : 1). Removing the solvent from the yellow fraction resulted in a yellow powder of **36**. ^{1}H NMR (DMSO-*d*$_6$) δ: 1.20–1.80 (m, 16H, Cy, Me); 2.25 (s, 12H, Me(dmgH)); 3.65 (m, br, 1H, *ipso*-H(Cy)); 9.85 (br, 1H, NH) ppm. IR (KBr) (cm^{-1}): 3175 (w) (NH); 2135 (s) (CN); 1645 (s), 1563 (s) (heterocycle). MS (pos-FAB) *m/z* (rel int. (%)): 509 (8) [Co(CN)(dmgH)$_2$L + H]$^+$; 483 (5) [Co(dmgH)$_2$L]$^+$; 195 (32) [L]$^+$.

For elemental analyses and physical properties, see Table 6.

3.9. *General procedure for the preparation of complexes* **37–39**

To a stirred solution of 1.5 mmol of N^{n}Bu$_4$-[Co(CN)$_2$(dmgH)$_2$] in 30 ml of MeOH was added 1.5 mmol of aldehyde via a syringe followed by 1.5 mmol of isonitrile at ice-bath temperature. To this solution was added dropwise 1.5 mmol of amine hydrochloride in 20 ml of MeOH. The mixture was then allowed to warm to room temperature overnight. Silica gel was added and the mixture evaporated to dryness. The resulting powder was transferred to a chromatography column charged with silica gel (2 × 25 cm) and eluted with ethyl acetate. The yellow products could be recrystallized from dichloromethane/tetrahydrofurane.

Compound **37**: ^{1}H NMR (DMSO-d_6) δ: 0.70–1.90 (m, 10H, Cy); 2.15 (s, 12H, Me); 2.60 (m, 1H, *ipso*-H(Cy)); 5.65 (d, J = 7.5 Hz, 1H, NH); 6.80–7.45 (m, 10H, Ph); 10.45 (s, 1H, NH); 17.65 (s, 2H, OHO) ppm. IR (KBr) (cm^{-1}): 3258 (vs) (NH); 2141 (w) (CN); 1548 (vs) (heterocycle). MS (pos-FAB) m/z (rel. int. (%)): 633 (13) $[Co(CN)(dmgH)_2L + H]^+$; 606 (19) $[Co(dmgH)_2L]^+$; 317 (36) $[L]^+$.

Compound **38**: ^{1}H NMR (DMSO-d_6) δ: 0.80–75 (m, 10H, Cy); 2.10 (s, 12H, Me); 2.20 (s, 3H, Me(Tol)); 2.60 (m, 1H, *ipso*-H(Cy)); 5.50 (d, 1H, NH); 6.75–7.45 (m, 9H, Ph, Tol); 10.45 (s, 1H, NH); 17.65 (s, 2H, OHO) ppm. IR (KBr) (cm^{-1}): 3265 (vs) (NH); 2134 (w) (CN); 1557 (vs) (heterocycle). MS (pos-FAB) m/z (rel. int. (%)): 647 (6) $[Co(CN)(dmgH)_2L + H]^+$; 620 (11) $[Co(dmgH)_2L]^+$; 331 (37) $[L]^+$.

Compound **39**: ^{1}H NMR (CDCl$_3$) δ: 1.15 (m, 9H, C(Me)$_3$); 2.10 (s, 12H, Me); 2.25 (s, 3H, Me(Tol)); 3.35 (s, 1H, NH); 6.65–7.40 (m, 9H, Ph, Tol); 10.65 (s, 1H, NH) ppm. IR (KBr) (cm^{-1}): 3293 (vs) (NH); 2133 (w) (CN); 1559 (vs) (heterocycle). MS (pos-FAB) m/z (rel. int. (%)): 621 (3) $[Co(CN)(dmgH)_2L + H]^+$; 594 (8) $[Co(dmgH)_2L]^+$; 306 (16) $[L]^+$.

For elemental analyses and physical properties, see Table 6.

3.10. Preparation of **40**

To a stirred solution of 0.87 g (1.5 mmol) of N^nBu_4 $[Co(CN)_2(dmgH)_2]$ in 30 ml of MeOH was added 0.32 g (3.0 mmol) of benzaldehyde via a syringe followed by 0.33 g (3.0 mmol) of cyclohexyl isocyanide at ice-bath temperature. To this solution was added dropwise 0.38 g (3.0 mmol) of aniline hydrochloride in 20 ml of MeOH. The mixture was stirred at room temperature overnight. The green-yellow precipitate was collected on a D$_4$ frit and washed with a small amount of petroleum ether to give 0.21 g (0.16 mmol) of $[Co(dmgH)_2L_2]^+[Co(CN)_2(dmgH)_2]^-$. IR (KBr) (cm^{-1}): 3278 (s) (NH); 2131 (w) (CN); 1562 (vs) (heterocycle). MS (pos-FAB) m/z (rel. int. (%)): 924 (100) $[Co(dmgH)_2L_2]^+$; 606 (4) $[Co(dmgH)_2L]^+$; 318 (29) $[L]^+$. MS (neg-FAB) m/z (rel. int. (%)): 341 (100) $[Co(CN)_2(dmgH)_2]^-$.

For elemental analyses and physical properties, see Table 6.

Table 7
Crystallographic data collection parameters

	9	**27**
Crystal data		
Formula	$C_{19}H_{26}CrN_2O_6$	$C_{25}H_{22}CrN_4O_5$
Molecular weight (g mol^{-1})	430.47	510.47
Crystal size (mm)	2.4 × 0.7 × 0.5	0.42 × 0.15 × 0.32
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Cell parameters		
a (Å)	9.824(4)	11.088(11)
b (Å)	16.070(4)	21.372(17)
c (Å)	18.004(4)	11.518(8)
β (°)	103.05(2)	117.82(7)
U (Å^3)	2770	2414
Z	4	4
D_c (g cm^{-3})	1.249	1.402
Collection and refinement parameters		
Radiation λ (Å)	graphite-monochromated Mo Kα (λ = 0.71069 Å)	
μ (cm^{-1})	5.54	
Temperature (K)	293	293
Scan mode	ω-scan	ω-scan
2θ limits (°)	$4 \le 2\theta \le 50$	$4 \le 2\theta \le 50$
Total no. of reflections	5111	3314
No. data	4055 ($I \ge 2\sigma(I)$)	1143 ($I \ge 4\sigma(I)$)
No. parameters	414	337
R	0.062	0.046
R_w	0.048	0.046
Programs used	SHELXS-86XTAL 2.2, ORTEP	SHELXS-86, XTAL 3.0, DIFABS, ORTEP

3.11. Preparation of the 4-amino-5-hydroxy-1,5-diphenyl-Δ^3-imidazolin-2-ones 48 and 49

To a solution of 1.28 g (2.0 mmol) of pentacarbonyl {4-cyclohexylamino-1,5-diphenyl-Δ^4-imidazolin-2-ylidene}tungsten in 100 ml of acetone was added 20 ml of an aqueous solution of $KMnO_4$ (3.32 g, 21 mmol); spontaneous formation of manganese dioxide was observed. Then 0.99 g (2.4 mmol) of $Fe(NO_3)_3 \cdot 9H_2O$ was added in portions which resulted in gas evolution and warming of the reaction mixture. After stirring at room temperature for 7 d, the solution became colourless. MnO_2 was filtered off, extracted with methanol and the filtrate concentrated. The resulting light yellow solid was transferred to a chromatography column charged with SiO_2 (2 × 20 cm) and eluted with petroleum ether/diethyl ether (1:2) to give 580 mg (83%) of **48**. ^{1}H NMR (DMSO-d_6) δ: 1.00–1.88 (m, 10H, Cy); 3.63 (m, 1H, CH); 6.88–8.00 (m, 12H, Ph, NH, OH) ppm. ^{13}C NMR (60 MHz) (DMSO-d_6) δ: 24.6, 25.0, 31.4, 51.6 (Cy); 90.2 (C5); 122.6–137.9 (aromatic-C); 162.0 (C4); 177.2 (C2). IR (KBr) (cm^{-1}): 3400 (w) (OH); 3221 (m) (NH); 3059 (m), 2929 (s), 2852 (m) (CH); 1707 (vs) (C=O) ppm. MS (EI) m/z (rel. int. (%)): 3.49 (22) (M^+); 333 (6.8) ($M^+ - O$); 257 (61.3) ($M^+ - Ph - O$).

Compound **49** was synthesized analogously to the procedure described for **48** with a yield of 82% by starting from pentacarbonyl{4-t-butylamino-1,5-diphenyl-Δ^4-imidazolin-2-ylidene}chromium. ^{1}H NMR (DMSO-d_6) δ: 1.32 (s, 9H, ^{t}Bu); 6.92–7.40 (m, 11H, Ph, OH); 7.50 (s, 1H, NH) ppm. ^{13}C NMR (60 MHz) (DMSO-d_6) δ: 28.5, 53.7 (^{t}Bu); 92.1 (C5); 124.6–138.5 (aromatic-C); 166.1 (C4); 177.7 (C2). IR (KBr) (cm^{-1}): 3398 (w) (OH); 3220 (m) (NH); 3059 (s), 2975 (m) (CH); 1710 (s) (C=O). MS (EI) m/z (rel. int. (%)): 323 (85) (M^+); 321 (53) ($M^+ - Ph - NH$).

For elemental analyses and physical properties, see Table 6.

3.12. X-ray structure determinations

Single crystals of **9** were grown from a concentrated solution in dimethyl sulfoxide, those of **27** by cooling a saturated solution in petroleum ether/diethyl ether. Crystals of suitable size were mounted in glass capillaries. Crystal data and data collection parameters for **9** and **27** are summarized in Table 7.

The intensity data were collected at 293 K on a STOE four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). All data were corrected for Lorentz polarization effects during the final stages of data reduction. The structures were solved by employing a combination of direct methods and different Fourier techniques with scattering factors for neutral atoms taken from the literature [37]. An absorption correction was carried out for **27**. Calculations were carried out on a VAX computer using the programs SHELXS-86 [38], XTAL 2.2/3.0 [39], DIFABS [40] and ORTEP [41]. After the non-hydrogen atoms had been located and refined, the hydrogen atoms were placed in positions suggested by the difference Fourier maps. Final refinements included anisotropic thermal parameters for all non-hydrogen atoms and isotropic ones for the hydrogen atoms. The full matrix least-squares refinements were based on F, and the functions minimized $\Sigma w(|F_o| - |F_c|)^2$. Agreement factors are defined as $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$ and $R_w = [\Sigma w(\| F_o| - |F_c\|^2)/\Sigma(w|F_o|^2)]^{1/2}$, $w = 1/\{\sigma(F_o)\}^2$.

Table 8
Fractional atomic coordinates and thermal parameters (Å^2) of the non-hydrogen atoms of **9** [a]

Atom	x	y	z	U_{eq} [b]
Cr	0.15727(6)	0.81972(4)	0.55788(3)	0.0546
C1	0.1455(4)	0.8929(3)	0.6375(3)	0.073
C2	0.0564(5)	0.7391(3)	0.5979(3)	0.082
C3	0.1857(5)	0.7456(3)	0.4830(3)	0.080
C4	−0.0049(5)	0.8608(3)	0.4955(3)	0.087
C5	0.2588(5)	0.9031(3)	0.5221(3)	0.077
O1	0.1420(4)	0.9403(2)	0.6847(2)	0.12
O2	−0.0081(4)	0.6910(3)	0.6220(2)	0.13
O3	0.2046(4)	0.6986(3)	0.4381(2)	0.12
O4	−0.1060(4)	0.8870(3)	0.4573(2)	0.14
O5	0.3189(4)	0.9570(2)	0.5020(2)	0.12
C6	0.3393(4)	0.7769(2)	0.6256(2)	0.053
N1	0.4573(3)	0.8212(2)	0.6524(2)	0.050
O6	0.3547(2)	0.6963(2)	0.6485(1)	0.062
C7	0.5513(3)	0.7696(2)	0.6938(2)	0.047
N2	0.6794(3)	0.7896(2)	0.7291(2)	0.050
C8	0.4948(4)	0.6830(2)	0.6957(2)	0.055
C9	0.4810(6)	0.6582(4)	0.7758(3)	0.077
C10	0.5705(5)	0.6187(3)	0.6593(3)	0.065
C11	0.5909(5)	0.6386(3)	0.5803(3)	0.074
C12	0.6755(6)	0.5729(4)	0.5499(3)	0.084
C13	0.7052(7)	0.5909(5)	0.4746(4)	0.11
C14	0.7977(7)	0.5250(5)	0.4501(4)	0.16
C15	0.833(2)	0.5493(9)	0.376(1)	0.24
C16	0.7408(4)	0.8752(2)	0.7313(2)	0.056
C17	0.6556(6)	0.9345(3)	0.7684(3)	0.076
C18	0.8876(5)	0.8679(4)	0.7803(4)	0.081
C19	0.7459(6)	0.9020(4)	0.6510(3)	0.080
S1	0.5328(2)	0.1125(1)	0.6419(1)	0.070
S2	0.4841(3)	0.1769(2)	0.6620(2)	0.070
O20	0.6477(3)	0.1605(2)	0.6899(2)	0.097
C21	0.4557(8)	0.1782(6)	0.5644(4)	0.12
C22	0.399(1)	0.1155(9)	0.6907(5)	0.17

[a] Standard deviations in parentheses. [b] $U_{eq} = 1/3 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Fractional atomic coordinates and thermal parameters of the non-hydrogen atoms for structures **9** and **27** are listed in Tables 8 and 9, respectively.

4. Supplementary material available

Further details of the crystal structure determinations may be obtained upon request from the Fachin-

Table 9
Fractional atomic coordinates and thermal parameters (Å^2) of the non-hydrogen atoms of **27** [a]

Atom	x	y	z	U_{eq} [b]
Cr	0.3356(2)	0.7468(1)	0.6507(2)	0.334(8)
C1	0.220(2)	0.8115(6)	0.644(1)	0.053(8)
C2	0.287(1)	0.7702(5)	0.475(1)	0.042(7)
C3	0.489(1)	0.8003(6)	0.713(1)	0.046(7)
C4	0.193(1)	0.6892(6)	0.591(1)	0.040(7)
C5	0.373(1)	0.7324(5)	0.825(1)	0.044(7)
C6	0.459(1)	0.6707(6)	0.658(1)	0.041(7)
C7	0.509(1)	0.6890(5)	0.472(1)	0.040(7)
C8	0.43(1)	0.6687(6)	0.348(1)	0.041(6)
C9	0.426(1)	0.7034(7)	0.243(1)	0.054(8)
C10	0.494(2)	0.7605(8)	0.269(2)	0.064(9)
C11	0.572(1)	0.7818(6)	0.396(2)	0.057(7)
C12	0.581(1)	0.7458(7)	0.502(1)	0.044(6)
C13	0.586(1)	0.5940(5)	0.621(1)	0.034(6)
C14	0.668(1)	0.5637(6)	0.567(1)	0.038(6)
C15	0.730(1)	0.5946(6)	0.502(1)	0.048(7)
C16	0.803(1)	0.5579(7)	0.456(1)	0.050(8)
C17	0.815(1)	0.4952(7)	0.479(1)	0.055(8)
C18	0.755(1)	0.4682(7)	0.548(1)	0.049(8)
C19	0.560(1)	0.5739(5)	0.718(1)	0.035(6)
C20	0.666(1)	0.5148(6)	0.929(1)	0.040(7)
C21	0.661(1)	0.4498(6)	0.973(1)	0.046(7)
C22	0.740(1)	0.4413(7)	1.121(1)	0.059(8)
C23	0.886(2)	0.4619(7)	1.170(1)	0.062(8)
C24	0.892(2)	0.5299(7)	1.128(1)	0.069(9)
C25	0.811(1)	0.5361(6)	0.978(1)	0.047(7)
N1	0.4850(9)	0.6200(4)	0.7408(9)	0.035(5)
N2	0.5211(9)	0.6538(4)	0.5849(9)	0.034(5)
N3	0.680(1)	0.5007(4)	0.5906(9)	0.042(5)
N4	0.587(1)	0.5173(5)	0.7825(9)	0.042(5)
O1	0.155(1)	0.8535(5)	0.641(1)	0.078(7)
O2	0.2537(9)	0.7912(4)	0.3720(9)	0.053(5)
O3	0.580(1)	0.8349(4)	0.752(1)	0.065(6)
O4	0.099(1)	0.6549(4)	0.553(1)	0.065(6)
O5	0.392(1)	0.7273(5)	0.933(1)	0.081(6)

[a] Standard deviations in parentheses. [b] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

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