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A novel reaction of the cyano ligand opening an organometallic route to 4-amino imidazoles: four component condensation (4CC) with isocyanide, aldehyde and amine*

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Abstract

Cyano complexes ($NEt_4[M(CN)(CO)_5]$, M = Cr, Mo, W), isocyanides (CNR^1, R^1 = Me, Bu^t, Cy, Tol^p), aldehydes (R^2CHO, R^2 = e.g. Ph, Tol^p, $C_6H_4NMe_2$-*p*, C_6H_4Cl-*p*) and amine hydrochlorides ($R^3NH_3^+Cl^-$, R^3 = H, Pr^i, Ph, Bz) undergo one-pot, four-component condensation type reactions (4CCs) to give the 4-aminoimidazolin-2-ylidene complexes $[M(CO)_5\{\overline{CN(H)C(NHR^1)C(R^2)N}R^3\}]$ (**1**–**24**). These include species which have further been functionalized in the 5-position by employing heteroaromatic (2-furanyl, 2-pyrrolyl, 2-thienyl, 2-pyridyl, 2-indenyl) and S-functional (2-thiomethoxyethyl) aldehydes, as well as dinuclear bisheterocycle-bridged ones obtained from dialdehydes (propanedial-1,3) or diamines (e.g. 1,2-diaminoethane, 1,4-diaminobenzene), respectively. Hydrazine in the place of amine gives rise to the carbenoid 1-(*N*-imino)-4-aminoimidazoles **25**–**28**, products of the incorporation into the heterocycle of *in situ* formed hydrazones as fourth components. The claimed nature of the complexes **1**–**28** is confirmed by an X-ray structure analysis of **28** which reveals a largely planar five-membered heterocycle with little delocalization between the Mo–C1(N1)N2–carbene and C7–C8 π-systems. Mechanistically, the organometallic 4CCs proceed according to their organic analogues which lead to hydantoin-4-imides; with $H[Co(CN)_2(dmgH)_2]$ as acid component, however, a salt-like product was obtained, the X-ray structure analysis of which revealed the presence of an amidinium type cation made up from the carbonyl, isocyanide and two amine components, and of an unchanged complex cyanocobalt counteranion. Detachment of the heterocyles from the complex has been achieved either oxidatively with $KMnO_4/Fe(NO_3)_3$ to give the 4-amino-5-hydroxo-imidazolin-2-one **33**, or through substitution with pyridine to give the corresponding C2–H imidazole **34**.

Key words: Crystal structures; Imidazoles; Condensation reactions; Transition metal complexes; Cyano complexes

Introduction

Owing to its ready availability and its nature as a versatile C_1 and N_1 synthon, CN^- (HCN) has received numerous applications in organic chemistry including large-scale industrial processes [1], and there is now well established evidence that CN^- also played a determining role in the emergence of life [2].

In organometallic chemistry, however, the cyanide ligand is practically non-existent except perhaps in some catalyst systems, e.g. $[Co(CN)_5]^{3-}$, or in organocuprates, e.g. LiR·CuCN, where it is regarded a mere spectator ligand [3–6]. Also, amazingly little is known about the role of the nickel catalyst in hydrocyanation processes [1, 7].

In recent years, our constant interest in functionalized isocyanides and their metal complexes has prompted us to investigate the chemistry of the parent compound [M]CNH as well as that of its precursor [M]CN, which turned out to be remarkably rich, the major findings being (i) a high tendency to form strong hydrogen bridges of the type [M]CN···H···Y (Y = O- or N-donor, e.g. EtOH [8] or :NC[M] [9]), (ii) a variety of 1,2-additions to and [2 + 3]-cycloadditions with multiply bonded species and three-membered rings, respectively [10], (iii) a series of electrophilic acylations, cyanations and alkinylations to give novel functional isocyanides [11–13], (iv) the 'radical alkylation' as a particularly

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efficient method of CN activation [14, 15] and (v) the spontaneous cleavage of the CN triple bond in a diiron complex under very mild conditions [16].

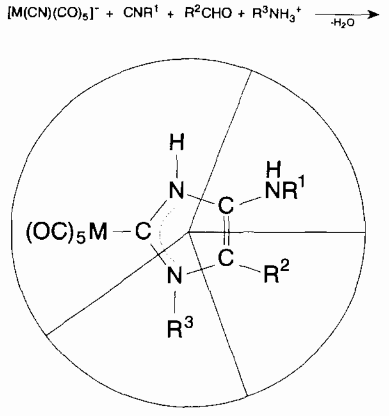
In this paper we report on a novel reaction of the metal coordinated and stabilized hydrogen isocyanide with three more components, an isocyanide, an aldehyde and an amine. It is only recently that multicomponent one-pot reactions (MCRs) enjoy greater popularity especially in the designation of strategies for the synthesis of natural products in which they prove superior to most multi-step processes as regards costs of work, time and material [17]. Lately, an MCR with seven (!) components (7CR) has been reported setting up an absolute record [18].

Hydrogen isocyanide complexes or, more conveniently, cyano complexes in the presence of some acid have already been tested in a 3CR with isocyanides and ketones and found to give rise to 4-aminooxazoline-2-ylidene complexes in high yields [19]. Now we present 28 4-aminoimidazoline-2-ylidene metal complexes including dinuclear diheterocyclic systems derived from diamines and dialdehydes, respectively, which have been synthesized by 4CC-type reactions (4CR). Furthermore, we demonstrate that the heterocycle is easily removed from the metal by substitution with pyridine.

Results and discussion

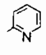
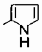
1. *Four component cycloadditions*

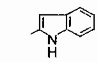
Mixing in methanol at 0 °C of equimolar amounts of the three reagents $[M(CN)(CO)_5]^-$ (M = Cr, Mo, W), CNR^1 (R^1 = e.g. Cy, Me, Bu^t Tol^p) and R^2CHO (R^2 = e.g. Ph, Pr^i, Tol^p), followed by slow addition of $R^3NH_3{}^+Cl^-$ (R^3 = e.g. Ph, H) resulted in a yellowish solution from which the imidazolin-2-ylidene complexes **1**–**12** were isolated in high yields (Scheme 1).

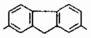

$$[M(CN)(CO)_5]^- + CNR^1 + R^2CHO + R^3NH_3{}^+ \xrightarrow[-H_2O]{}$$

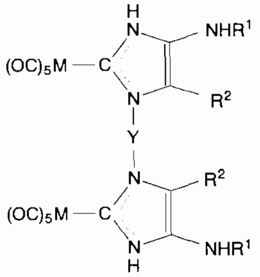
Scheme 1.

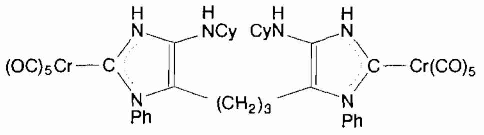
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
M	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Mo	W
R^1	Cy	Me	Bu^t	Bu^t	Bu^t	Tol^p	Cy	Cy	Bu^t	Bu^t
R^2	Ph	Ph	Ph	Ph	Ph	Tol^p	Tol^p	Ph	Ph	Ph
R^3	Ph	Ph	Ph	Pr^i	H	Ph	Ph	Bz	Ph	Ph

	11	**12**	**13**	**14**
M	W	W	Cr	Cr
R^1	Bu^t	Bu^t	Cy	Cy
R^2	$C_6H_4NMe_2$-*p*	C_6H_4Cl-*p*		
R^3	Ph	Ph	Ph	Ph

	15	**16**	**17**	**18**
M	Cr	W	W	W
R^1	Cy	Bu^t	Bu^t	Cy
R^2	$-CH_2CH_2SMe$		$-CH_2CH_2SMe$	
R^3	Ph	Ph	Ph	Ph

	M	R^1	R^2	Y
19	Cr	Bu^t	Ph	
20	Cr	Bu^t	Ph	$-CH_2CH_2-$
21	Cr	Cy	Ph	
22	W	Bu^t		
23	W	Cy	Ph	





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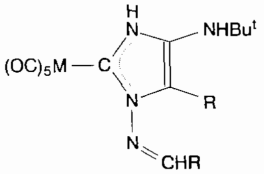
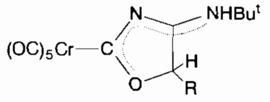
Changing the order of addition of the components has no influence on the results. Carbenoid imidazoles carrying further functional groups in the 5-position (**13**–**18**) have been obtained by the use of the corresponding N-heteroaromatic and S-functional aldehydes, while diamines in the place of amines gave rise to the dinuclear bisheterocyclic systems **19**–**23** demonstrating the wide variability of components tolerated by this 4CC reaction of cyano complexes. Also, a dialdehyde was employed to give a second type of a bisheterocyclic dichromium compound (**24**). In another series of experiments, cyano chromium and molybdenum species were reacted with aldehyde, t-butylisocyanide and, in the place of the primary amine, hydrazine. Still, the result again was 4-aminoimidazolin-2-ylidene type complexes **25**–**28**, in the formation of which, however, a second molecule of aldehyde had been involved thereby establishing some kind of 5CC. This variant may be rationalized by assuming that, in a preceding step, hydrazine and the carbonyl component give rise to the corresponding hydrazone which with its free NH_2 function takes over the part of the primary amine (cf. 4.).

The colorless to pale yellow substances are soluble in most organic solvents. The solutions turn out to be quite air-sensitive, taking on a brownish color within minutes. In the solid state, however, the new complexes except **25**–**28** are air-stable.

During chromatographic work-up of **26**, a second band separated which contained a pale yellow side product (**29**) obviously resulting from a three-component cycloaddition of pentacarbonyl(hydrogen isocyanide)chromium, t-butyl isocyanide and isobutyraldehyde. This type of reaction has already been dealt with by us in a preliminary paper [19].

	M	R
25	Cr	Ph
26	Cr	Pr^i
27	Cr	Et
28	Mo	Ph





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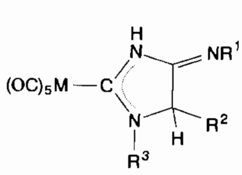
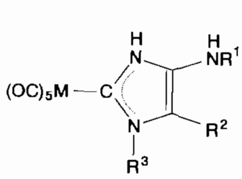
Other N-nucleophiles such as hydroxylamine and semicarbazide have been tried as substitutes for the primary amine, however, with no success. The reaction with semicarbazide merely gave semicarbazone, while in the other cases, the products have not been identified.

2. Spectroscopic studies

The first point in question was which type of tautomer, **A** or **B**, would more properly describe the carbenoid imidazole species in the complexes **1**–**28**. While the IR spectra with their two medium to strong ν(NH) absorptions between 3450 and 3350 cm^{-1} were already in favor of form **B**, unequivocal proof for **B** came from ^1H NMR spectroscopy (Tables 1 and 2). Here, as a rule, two broad signals are found around 3 and 8–9 ppm, both of which disappear on addition of D_2O thus disclosing their nature as exchangeable NH protons. Also, in complexes **1**, **14**, **15**, **18**, **21**, **23** and **24**, the high field NH resonance is clearly a doublet which arises from coupling with the *gem*-H of the cyclohexyl group (Table 2).



A



B

Further IR characteristics of the pentacarbonyl(imidazolin-2-ylidene)metal-6 complexes are exceptionally narrow, sharp $\nu(CO)_e$ [A_1] bands and particularly low energy $\nu(CO)_e$ [E] bands (Table 1), the latter providing clear evidence for the strong electron donating properties of this carbene ligand. The so-called carbene absorption, $\nu_{as}(N\overset{...}{=}C\overset{...}{=}N)$, which predominates in the spectra of open-chain N,N'-carbenes and saturated carbenoid heterocycles [20] as a very strong and broad band somewhere around 1500 cm^{-1}, cannot be assigned with certainty. In aromatic systems like the one on hand, this region only exhibits medium or low intensity bands including $\nu(C=C)$ species. The medium to strong absorptions about 1600 and 1650 cm^{-1} present in all compounds, on the other side, are expected to contain a substantial contribution of $\nu_{as}(N\overset{...}{=}C\overset{...}{=}N)$ character due to the extensive coupling of this motion with other ring vibrations; in addition some δ(NH) character has probably been mixed in. The stretching mode of the exocyclic 1-(*N*-imino) group of the 5CC products **25**–**28** obviously absorbs with the same frequency.

The particularly interesting ^{13}C NMR chemical shifts of the carbene carbon atoms have unequivocally been established by use of a ^{13}C labeled 4CC product synthesized from $[Cr(^{13}CN)(CO)_5]^-$. They range between 170 and 190 ppm, i.e. correspond to substantially higher fields than those of the Fischer-type alkoxy and aminocarbene complexes ($\delta \sim 300$–360 ppm) [21], the 3CC products $[\mathrm{Cr(CO)_5\{\overline{CNC(NHR^1)CR^2R^3O}\}}]$ ($\delta \sim 270$ ppm) [19], and even the saturated cyclic diaminocarbene species, e.g. $[\mathrm{Cr(CO)_5\{\overline{CN(R)CH_2CH_2NH}\}}]$ ($\delta \sim 220$ ppm) [22, 23], in which the carbene-C signal almost coincides with that of the axial CO ligand. For the closely related pentacarbonyl(N,N'-dimethylimidazolin-2-ylidene)tungsten, on the other hand, a very similar value, δ 180.5 ppm, has been found [24].

Of the two other ring carbon atoms, the signals fall into the range of phenyl resonances (C5) or, respectively, appear slightly outside their low field limit (C4) allowing for an identification. The hydrazono carbon of **25**–**27** is at resonance at a distinctly lower field (Table 2).

The mass spectra of the mononuclear complexes typically show the molecular peaks and the successive loss of five CO ligands with the carbonyl-free $[ML]^+$ frequently being the base peak. Also, the metal-free imidazole is observed in most cases. In the EI spectra

TABLE 1. Selected IR data for the complexes **1**–**28** (cm^{-1}) (KBr)

Complex	ν(NH)	ν(CO)	Others[a]
1	3317w	2051s, 1904vs,br	1655m, 1597m
2	3445s, 3423m	2053vs, 1965vs, 1905vs,br, 1853vs	1665s, 1598m
3	3451s	2053vs, 1957vs, 1893vs,br	1645s, 1596m
4	3462s, 3398m	2052s, 1940sh, 1902vs, 1871vs	1638s, 1595m
5	3469m, 3405s	2057s, 1973s, 1939s, 1909vs, 1872s, 1857s	1654m, 1598m
6	3425m	2054s, 1967s, 1913vs,br	1658m, 1608m
7	3435m, 3423m	2053vs, 1884vs	1651s
8	3435vs, 3358w	2054vs, 1915vs, 1865vs	1658s, 1598m
9	3449s	2060s, 1962s, 1892vs,br	1640m, 1596m
10	3445s	2059s, 1954s, 1902vs, 1883vs,br	1640m, 1596m
11	3443s, 3350w	2059vs, 1983vs, 1955vs	1648m, 1608m
12	3435s, 3349w	2059vs, 1908vs	1640s, 1594s
13	3459s	2051vs, 1957vs, 1894vs	1633s, 1586s
14	3436s, 3359s	2054vs, 2001vs, 1974vs, 1917vs	1657s, 1596m
15	3321w, 3187m	2051vs, 1957s,sh, 1900vs	1654m, 1595m
16	3441s	2053vs, 1965vs	1645s, 1597m
17	3330s	2060vs, 1900vs	1630s
18	3338m, 3166m	2059vs, 2001vs, 1991vs, 1897vs	1649m, 1596m
19	3427s, 3353w	2054s, 1965s, 1899s,br	1640m, 1597m
20	3443m	2055s, 1965s,sh, 1902vs,br	1640m, 1598w
21	3441s	2053vs, 1965vs	1645s, 1597m
22	3431s, 3364m	2060vs, 2001vs, 1894vs	1643s, 1560s
23	3427m	2060vs, 1903vs	1646s, 1597m
24	3441s, 3350w	2053vs, 2001vs, 1894vs	1656s, 1596m
25	3390s	2057m, 1968s, 1955vs, 1932vs, 1809m	1630m
26	3444m, 3367w	2054s, 1965s, 1940vs, 1920vs, 1865vs	1631m
27	3439s, 3362w	2054s, 1968s, 1936vs, 1905vs, 1845s	1635m
28	3437s	2059s, 1965s, 1884s,br	1638m

[a]Characteristic vibrations of the heterocyclic ligand.

of the dinuclear species **19** and **20**, however, the molecular peaks are missing. Here, the highest masses are those of the free bisheterocycle (**19**) or of the monochromium complex thereof (**20**). The latter ion also causes the highest intensity line in the pos-FAB spectrum of **20**. In addition, this spectrum shows an $[M_2(CO)_{10}L+H]^+$ peak followed by fragments containing fewer or no CO ligands (Table 3).

3. X-ray structure of 28

An ORTEP drawing of the molecular structure of a 4CC product with, formally, phenylhydrazone in the place of the primary amine, viz. **28**, is shown in Fig. 1; pertinent bond lengths and angles are given in Table 4. The findings fully confirm the formulations of **1**–**28** as carbenoid metal–carbon bonded imidazoles with amino (NHR) substituents in the 4-position. The molybdenum to carbene carbon bond distance is by far the longest of the six Mo–C bonds in **28**, the Mo–C(O)$_{trans}$, accordingly, belongs to the shortest, though it is not significantly shorter than the average Mo–C(O) distance. Of the few Mo–C(carbene) bond lengths reported in the literature, those of *cis*-$[Mo(CO)_4\{\overline{CN(Me)CH_2CH_2N}Me\}_2]$ (2.293(3) Å [25] and *trans*-$[Mo(CO)_4\{\overline{CN(Me)CH_2CH_2N}Me\}_2]$ (2.232(2) Å) [26] are in reasonable agreement with the value determined in this study.

The most proper description of the structure of **28** is that of a central, largely planar five-membered heterocycle carrying four sterically demanding substituents of which the pentacarbonylmolybdenum group is rotated to such a degree that the ring plane is staggered with respect to the *cis*-CO ligands; the phenyl ring in 5-position is almost coplanar, while the 1-(*N*-phenylimino) substituent, perfectly planar in itself, adopts a kind of *gauche* conformation thus ruling out any π-interaction with the imidazole (Table 4).

Within the heterocycle, in spite of its aromaticity, there is no uniformity of bond distances nor is there any sequence of like bond lengths as, for example, in the structures of 3CC products [19, 27]. One rather observes markedly different bond lengths reflecting the existence of two more or less localized π-systems, viz. the bisheteroatom-stabilized metal–carbene moiety and the transannular C–C double bond, tied together by relatively long (C–N) bonds. In the course of our work on homoleptic carbene complexes, e.g. $[Pd\{\overline{CN(Me)CHCHN}H\}_4]I_2$ [28], and [3+2]-cycloadditions with metallo nitrile ylides, e.g. $NEt_3H[W(CO)_5\{\overline{CN(H)C(CO_2Et)C(O^-)N}Ph\}]$ [29], we

TABLE 2. ^{1}H and ^{13}C NMR data for complexes **1–27**[a]

Complex	Solvent	^{1}H NMR	^{13}C NMR
1	CDCl$_3$	1.04–2.04 (c, 10H, C$_6$H$_{10}$), 3.00 (m, 1H, *ipso*-H(Cy)), 3.24 (d, 1H, NH), 7.00–7.38 (m, 10H, Ph), 8.88 (s, 1H, NH)	24.7, 25.5, 33.9, 56.1 (Cy), 121.3–135.2 (Ph + C5), 139.6 (C4), 186.7 (carbene C), 217.7 (CO$_{eq}$), 221.7 (CO$_{ax}$)
2	CDCl$_3$	2.88 (d, 3H, Me), 3.50 (s, 1H, NH), 6.94–7.40 (m, 10H, Ph), 9.04 (s, 1H, NH)	33.9 (Me), 118.9–137.4 (Ph + C5), 139.4 (C4), 186.3 (carbene C), 217.7 (CO$_{eq}$), 221.6 (CO$_{ax}$)
3	CDCl$_3$	1.16 (s, 9H, CMe$_3$), 3.14 (s, 1H, NH), 6.94–7.32 (m, 10H, Ph), 8.88 (s, 1H, NH)	30.0 (C(*C*H$_3$)$_3$), 54.1 (*C*Me$_3$), 125.8–133.6 (Ph + C5), 139.5 (C4), 187.7 (carbene C), 217.7 (CO$_{eq}$), 221.7 (CO$_{ax}$)
4	CDCl$_3$	1.06 (d, 6H, CMe$_2$), 1.28 (s, 9H, CMe$_3$), 2.70 (m, 1H, NH), 7.20–7.52 (m, 5H, Ph), 8.64 (s, 1H, NH)	21.6 (HC(*C*H$_3$)$_2$), 24.8 (H*C*Me$_2$), 30.4 (C(*C*H$_3$)$_3$), 53.2 (*C*Me$_3$), 129.1–130.9 (Ph + C5), 139.8 (C4), 186.6 (carbene C), 217.8 (CO$_{eq}$), 221.9 (CO$_{ax}$)
5	CDCl$_3$	1.18 (s, 9H, CMe$_3$), 3.08 (s, 1H, NH), 7.32–7.50 (m, 5H, Ph), 8.68 (s, 1H, NH), 8.92 (s, 1H, NH)	30.1 (C(*C*H$_3$)$_3$), 54.5 (*C*Me$_3$), 123.0–129.3 (C5), 132.3 (C4), 186.5 (carbene C), 218.1 (CO$_{eq}$), 221.5 (CO$_{ax}$)
6	CDCl$_3$	2.22 (s, 3H, Ph-CH$_3$), 2.30 (s, 3H, Ph-CH$_3$), 5.18 (s, 1H, NH), 6.64–7.42 (m, 13H, Ph), 9.24 (s, 1H, NH)	20.5 (Ph-*C*H$_3$), 21.1 (Ph-*C*H$_3$), 114.6–139.5 (Ph + C5), 141.9 (C4), 190.3 (carbene C), 217.5 (CO$_{eq}$), 221.6 (CO$_{ax}$)
7	CDCl$_3$	0.88–1.70 (m, 10H, C$_6$H$_{10}$), 2.93 (m, 1H, *ipso*-H(Cy)), 3.65 (s, 3H, Me), 4.25 (d, J = 6 Hz, 1H, NH), 6.70–7.35 (m, 9H, Ph), 11.80 (s, 1H, NH)	24.2, 26.3, 33.0, 53.4 (Cy), 54.9 (OMe), 113.3–139.5 (aromatic C + C5), 158.4 (C4), 179.1 (carbene C), 217.6 (CO$_{eq}$), 222.1 (CO$_{ax}$)
8	CDCl$_3$	1.00–2.00 (m, 10H, C$_6$H$_{10}$), 2.92 (m, 1H, *ipso*-H(Cy)), 2.96 (s, 1H, NH), 5.25 (s, 2H, CH$_2$N), 6.80–7.25 (m, 10H, Ph), 8.80 (s, 1H, NH)	24.7, 25.5, 33.9, 52.5 (Cy), 56.1 (CH$_2$N), 119.9–135.9 (aromatic C + C5), 136.9 (C4), 185.2 (carbene C), 217.8 (CO$_{eq}$), 221.5 (CO$_{ax}$)
9	CDCl$_3$	1.16 (s, 9H, CMe$_3$), 6.96–7.36 (m, 10H, Ph), 3.18 (s, 1H, NH), 8.88 (s, 1H, NH)	30.0 (C(*C*H$_3$)$_3$) 54.2 (*C*Me$_3$), 124.7–133.3 (Ph + C5), 140.0 (C4), 182.9 (carbene C), 206.4 (CO$_{eq}$), 212.0 (CO$_{ax}$)
10	CDCl$_3$	1.08 (s, 9H, CMe$_3$), 3.10 (s, 1H, NH), 6.88–7.28 (m, 10H, Ph), 8.80 (s, 1H, NH)	30.0 (C(*C*H$_3$)$_3$), 54.2 (*C*Me$_3$), 124.5–133.6 (Ph + C5), 139.9 (C4), 173.9 (carbene C), 198.0 (CO$_{eq}$, J = 125 Hz), 201.6 (CO$_{ax}$)
11	DMSO-d$_6$	0.90 (s, 9H, CMe$_3$), 2.80 (s, 6H, NMe$_2$), 3.78 (s, 1H, NH), 6.45–7.35 (m, 9H, Ph), 12.10 (s, 1H, NH)	29.5 (C(*C*H$_3$)$_3$), 29.4 (NMe), 53.4 (*C*Me$_3$), 111.2–140.3 (aromatic C + C5), 149.2 (C4), 168.2 (carbene C), 198.0 (CO$_{eq}$), 202.3 (CO$_{ax}$)
12	DMSO-d$_6$	0.90 (s, 9H, CMe$_3$), 4.10 (s, 1H, NH), 7.20–7.45 (m, 9H, Ph), 12.25 (s, 1H, NH)	29.5 (C(*C*H$_3$)$_3$), 53.7 (*C*Me$_3$), 124.7–134.0 (aromatic C + C5), 139.8 (C4), 170.0 (carbene C), 197.9 (CO$_{eq}$), 202.2 (CO$_{ax}$)
13	CDCl$_3$	1.00–2.00 (m, 10H, C$_6$H$_{10}$), 3.28 (m, 1H, *ipso*-H(Cy)), 3.43 (d, 1H, NH), 5.75–8.35 (m, 9H, Ph + pyridyl), 8.70 (s, 1H, NH)	24.3, 25.4, 33.7, 52.8 (Cy), 40.5 (CH$_2$), 117.1–148.2 (Ph + pyridyl + C5), 149.9 (C4), 188.1 (carbene C), 217.5 (CO$_{eq}$), 221.6 (CO$_{ax}$)
14	CDCl$_3$	1.00–1.75 (m, 10H, C$_6$H$_{10}$), 2.75 (m, 1H, *ipso*-H(Cy)), 4.45 (d, J = 6 Hz, 1H, NH), 5.65–7.30 (m, 8H, Ph + pyrrolyl), 10.70 (s, 1H, NH), 11.71 (s, 1H, NH)	24.3, 25.1, 33.1, 52.5 (Cy), 107.6–137.6 (Ph + pyrrolyl + C5), 139.6 (C4), 178.6 (carbene C), 217.6 (CO$_{eq}$), 222.1 (CO$_{ax}$)
15	CDCl$_3$	1.05–2.50 (m, 17H, C$_6$H$_{10}$ + SMe + (CH$_2$)$_2$), 2.93 (m, 1H *ipso*-H(Cy)), 3.10 (d, J = 6 Hz, 1H, NH), 7.20–7.50 (m, 5H, Ph), 8.71 (s, 1H, NH)	24.7, 25.3, 25.6, 27.1 (Cy), 23.7, 33.4, 34.2 ((CH$_2$)$_2$SMe), 129.3–129.9 (Ph + C5), 136.6 (C4), 170.0 (carbene C), 216.5 (CO$_{eq}$), 217.7 (CO$_{ax}$)
16	DMSO-d$_6$	1.95 (s, 9H, CMe$_3$), 3.68 (s, 1H, NH), 6.83–7.33 (m, 10H, Ph + indenyl), 11.15 (s, 1H, NH), 12.15 (s, 1H, NH)	29.4 (C(*C*H$_3$)$_3$), 53.2 (*C*Me$_3$), 102.3–135.5 (Ph + indenyl + C5), 140.4 (C4), 168.7 (carbene C), 198.1 (CO$_{eq}$, J_{CW} = 63 Hz), 202.3 (CO$_{ax}$)

(continued)

TABLE 2. (*continued*)

Complex	Solvent	^{1}H NMR	^{13}C NMR
17	$CDCl_3$	1.18 (s, 9H, CMe_3), 1.83 (s, 3H, SMe), 2.23 (t, 2H, CH_2), 2.50 (t, 2H, CH_2), 3.10 (s, 1H, NH), 7.18–7.45 (m, 5H, Ph), 8.68 (s, 1H, NH)	15.5 ($C(\mathit{C}H_3)_3$), 23.8, 30.7, 33.5 ($(CH_2)_2SMe$), 53.6 ($\mathit{C}Me_3$), 123.5–132.8 (aromatic C + C5), 139.5 (C4), 173.9 (carbene C), 198.0 (CO_{eq}, $J_{CW} = 63$ Hz), 201.6 (CO_{ax})
18	DMSO-d_6	0.95–1.78 (m, 10H, C_6H_{10}), 3.13 (m, 1H, *ipso*-H(Cy)), 4.58 (d, $J = 10$ Hz, 1H, NH), 6.88–7.45 (m, 8H, Ph + thienyl), 11.93 (s, 1H, NH)	24.4, 25.2, 33.1, 53.2 (Cy), 109.9–137.6 (aromatic C + thienyl + C5), 139.5 (C4), 168.7 (carbene C), 197.9 (CO_{eq}, $J_{CW} = 31$ Hz), 202.0 (CO_{ax})
19		not measured	not measured
20	DMSO-d_6	0.78 (s, 18H, CMe_3), 3.68 (s, 2H, NH), 4.08 (m, br, 4H, CH_2CH_2), 7.08–7.46 (m, 10H, Ph)	29.3 ($C(\mathit{C}H_3)_3$), 49.3 ($(CH_2)_2$), 53.3 ($\mathit{C}Me_3$), 125.1–129.7 (Ph + C5), 134.5 (C4), 180.4 (carbene C), 217.2 (CO_{eq}), 222.2 (CO_{ax})
21	DMSO-d_6	1.00–1.69 (m, 20H, C_6H_{10}), 2.90 (m, 2H, *ipso*-H(Cy)), 3.76 (s, 2H, CH_2-ring), 4.34 (d, $J = 10$ Hz, 2H, NH), 7.14–7.83 (m, 16H, Ph + fluorenyl), 11.83 (s, 2H, NH)	24.3, 25.2, 32.9, 53.5 (Cy), 40.5 (CH_2), 119.0–140.2 (Ph + fluorenyl + C5), 143.5 (C4), 180.1 (carbene C), 217.6 (CO_{eq}), 222.0 (CO_{ax})
22	DMSO-d_6	1.00 (s, 18H, CMe_3), 4.10 (s, 2H, NH), 6.00–7.50 (m, 10H, C_6H_4, furanyl), 12.20 (s, 2H, NH)	[b]
23	DMSO-d_6	1.00–1.75 (m, 20H, C_6H_{10}), 3.00 (m, 2H, *ipso*-H(Cy)), 4.30 (d, $J = 6$ Hz, 2H, NH), 7.00–7.28 (m, 14H, C_6H_4, Ph), 12.00 (s, 2H, NH)	24.3, 25.2, 33.0, 53.6 (Cy), 117.9–136.1 (aromatic C + C5), 140.0 (C4), 197.9 (carbene C), 281.6 (CO_{eq}), 294.0 (CO_{ax})
24	DMSO-d_6	0.79–2.00 (m, 26H, $C_6H_{10} + (CH_2)_3$), 2.85 (m, 2H, *ipso*-H(Cy)), 3.00 (d, $J = 7$ Hz, 2H, NH), 7.28–7.50 (m, 10H, Ph), 11.71 (s, 2H, NH)	22.1 ($CH_2\mathit{C}H_2CH_2$), 24.5, 25.5, 33.2, 54.6 (Cy), 65.4 ($\mathit{C}H_2CH_2\mathit{C}H_2$), 119.7–138.8 (Ph + C5), 145.0 (C4), 178.7 (carbene C), 217.6 (CO_{eq}), 222.2 (CO_{ax})
25	DMSO-d_6	1.11 (s, 9H, CMe_3), 3.30 (s, NH), 7.30–7.70 (m, 10H, Ph), 7.92 (s, 1H, N=CH), 9.70 (s, 1H, NH)	30.1 ($C(\mathit{C}H_3)_3$), 54.4 ($\mathit{C}Me_3$), 120.5 (C5), 132.2 (C4), 127.0–134.0 (Ph), 164.7 (C=N), 185.8 (carbene C), 218.3 (CO_{eq}), 222.5 (CO_{ax})
26	DMSO-d_6	1.25 (d, 6H, $(CH(\mathit{C}H_3)_2)$), 1.32 (d, 6H, $N{=}CHCH(\mathit{C}H_3)_2$), 2.81 (m, 1H, $(\mathit{CH}Me_2)$), 3.10 (m, $N{=}CH\mathit{CH}Me_2$), 1.20 (s, 9H, CMe_3), 3.86 (s, 1H, NH), 8.12 (d, 1H, N=CH), 11.36 (s, 1H, NH)	17.9, 20.8 (Me), 23.3, 31.7 (CH), 29.5 ($C(\mathit{C}H_3)_3$), 52.5 ($\mathit{C}Me_3$), 127.3 (C5), 131.0 (C4), 170.4 (C=N), 180.2 (carbene C), 217.9 (CO_{eq}), 222.4 (CO_{ax})
27	DMSO-d_6	0.95–1.25 (t, 6H, Me), 1.10 (s, 9H, CMe_3), 2.40–2.80 (m, 4H, (CH_2)), 3.94 (s, 1H, NH), 8.16 (t, 1H, N=CH), 11.52 (s, 1H, NH)	8.7, 12.2 (Me), 15.2, 25.8 (CH_2), 29.9 ($C(\mathit{C}H_3)_3$), 52.7 ($\mathit{C}Me_3$), 123.2 (C5), 131.6 (C4), 172.8 (C=N), 178.2 (carbene C), 218.2 (CO_{eq}), 222.8 (CO_{ax})

[a] Chemical shifts, δ, as ppm downfield from Me_4Si as internal standard. [b] Compound not soluble enough.

TABLE 3. Selected mass spectroscopic data (*m/z* (rel. intensity))

Complex	EI: $[M(CO)_5L]^+$ pos-FAB: $[M_2(CO)_{10}L+H]^+$	$[ML]^+$	$[L]^+$
EI (80 eV)			
1	509 (5)	369 (100)	317 (54)
2	441 (6)	301 (93)	249 (100)
3	483 (6)	343 (100)	291 (4)
4	449 (15)	309 (100)	257 (4)
5	407 (12)	267 (100)	
6	531 (18)	391 (100)	339 (55)
7	539 (3)	399 (66)	347 (100)
8	523 (6)	383 (44)	331 (82)
9	529 (10)	389 (62)	291 (69)
10	615 (22)	475 (42)	291 (4)
11	658 (0.4)	518 (1)	334 (33)
12	649 (13)	509 (32)	325 (73)
13	510 (5)	370 (74)	370 (100)
14	498 (6)	358 (55)	306 (100)
15	507 (0.9)	367 (24)	315 (23)
17	613 (28)	473 (27)	289 (39)
18	647 (2)	507 (3)	323 (94)
19			504 (14)
20		508 (9)	
28	556 (0.6)	416 (3)	318 (30)
pos-FAB			
16	654 (54)[a]	514 (26)	331 (100)
19		556 (5)	
20	841 (2)	508 (100)	
21	1029 (0.4)	748 (8)[b]	645 (15)
22	1133 (5)		485 (2)
23	1205 (27)		558 (27)
24	907 (7)	626 (44)[b]	574 (15)

[a] $[M(CO)_5L+H]^+$. [b] $[M_2L]^+$.

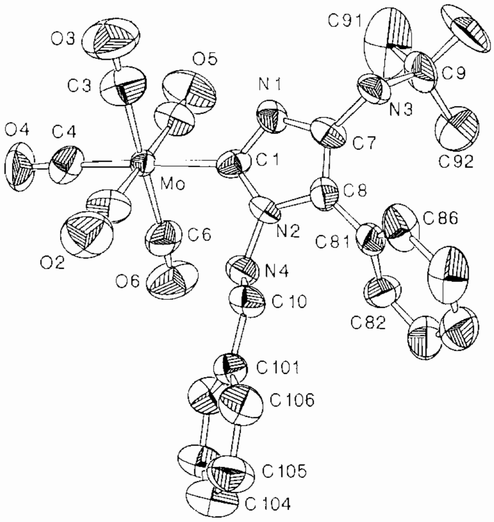


Fig. 1. ORTEP plot and labeling scheme of **28**. Hydrogen atoms have been omitted for clarity and the thermal ellipsoids have been drawn to include 50% probability.

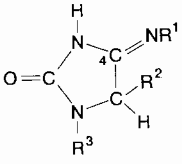
have repeatedly drawn attention to this structural characteristics which seem to be quite a common feature of C-metalated heterocycles [30].

As indicated by several relatively short intermolecular contacts particularly involving the atoms N1, N3 and O4 (Table 4), some hydrogen bonding probably occurs between the molecules of **28** though no hydrogen atoms have been located.

4. *Mechanistic considerations*

The organometallic three and four component condensations of hydrogen isocyanide complexes, isocyanides, carbonyl compounds and, in the case of 4CC, amines, have their precedent in Passerini's 3CR of the 1920s [31] and in Ugi's 4CC of 1959 [32]. These and related organic multicomponent reactions which are thought to proceed in a zipper-like manner, i.e. each reaction step is a prerequisite for the following, have only recently attracted full attention as extremely efficient one-pot syntheses particularly of complicated molecules including natural products such as various antibiotics [17].

The crucial step to all 4CCs is the α-addition to the isocyanide of an iminium ion (generated from a carbonyl compound $R'R''C{=}O$ and an amine RNH_2 in the presence of an acid HX) and a nucleophile (usually the acid anion X^-). Alternatively, isocyanide insertion into the C–X bond of the 'α-aminoalkylated' acid (RHN–CR'R''–X) has been envisaged. Subsequent coupling with secondary reactions leads to stable products [33]. Originally, carboxylic acids have been used as acid components to give acylated α-amino acid amides [32a]. Changing the acid changes the nature of the secondary reaction and with it the type of product. Thus, cyanic acid (HOCN) yields hydantoin-4-imides (**30**) and, accordingly, thiocyanic acid 2-thiohydantoin-4-imides [34], the starting materials and products of which are related to the metal-coordinated and -stabilized hydrogen isocyanide and 4-amino-imidazolin-2-ylidenes, respectively, through the isolobal analogy of oxygen (sulfur) atoms with d^6-ML_5 fragments – where M equals Cr(0) to W(0) and L equals CO – derived from octahedral transition metal complexes [35].



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As perhaps suggested by this relationship, the organometallic 4CCs proceed in much the same manner as their organic *vis-à-vis* as regards reaction conditions, substrates, selectivities and, obviously, also mechanism. According to this, preformed Schiff bases in the place of carbonyl compounds and amines, the use of which proved particularly advantageous in cases where side reactions occur [34], were also applied with success in

TABLE 4. Selected intermolecular contact distances, bond distances (Å), bond angles and dihedral angles (°) of **28**[a,b]

Intermolecular contact distances[c]			
O5···H106^{I}	2.68	O4···C5^{III}	3.304(17)
O6···H84^{I}	2.85	C3···O4^{III}	3.305(18)
N1···O4^{III}	2.927(14)	C83···O6^{III}	3.326(19)
N3···N3^{II}	3.072(14)	C7···N3^{II}	3.349(16)
O4···O3^{III}	3.297(15)	O6···C82^{III}	3.435(17)
Bond distances			
Mo–C1	2.211(11)	Mo–C2	1.932(15)
Mo–C3	1.941(14)	Mo–C4	1.933(12)
Mo–C5	1.970(14)	Mo–C6	2.000(13)
C2–O2	1.205(19)	C3–O3	1.197(17)
C4–O4	1.193(15)	C5–O5	1.174(17)
C6–O6	1.172(16)		
C1–N1	1.345(14)	C1–N2	1.346(13)
N1–C7	1.419(14)	C7–C8	1.359(14)
C8–N2	1.414(13)		
C7–N3	1.406(14)	N3–C9	1.526(15)
C9–C91	1.548(20)	C9–C92	1.530(18)
C9–C93	1.560(18)		
C8–C81	1.494(14)	C81–C82	1.471(16)
C82–C83	1.430(16)	C83–C84	1.421(24)
C84–C85	1.457(22)	C85–C86	1.467(20)
C86–C81	1.417(19)		
N2–N4	1.435(11)	N4–C10	1.314(14)
C10–C101	1.496(14)	C101–C102	1.429(18)
C102–C103	1.409(20)	C103–C104	1.412(20)
C104–C105	1.394(23)	C105–C106	1.443(18)
C106–C101	1.420(18)		
Bond angles			
C1–Mo–C4	177.8(4)		
C2–Mo–C5	178.5(5)		
C3–Mo–C6	178.5(6)		
Mo–C2–O2	180(1)	Mo–C3–O3	178(1)
Mo–C4–O4	179.2(9)	Mo–C5–O5	176(1)
Mo–C6–O6	176(1)	Mo–C1–N1	128.6(7)
Mo–C1–N2	128.9(8)		
N1–C1–N2	102.2(9)	C1–N2–C8	113.8(8)
N2–C8–C7	105.1(8)	C8–C7–N1	105.0(9)
C7–N1–C1	113.7(8)		
N1–C7–N3	123.1(9)	C8–C7–N3	132(1)
C7–N3–C9	118.1(9)	N3–C9–C91	111(1)
N3–C9–C92	109.1(9)	N3–C9–C93	101(1)
C91–C9–C92	112(1)	C91–C9–C93	116(1)
C92–C9–C93	108(1)		
C7–C8–C81	131.1(9)	N2–C8–C81	123.7(8)
C8–C81–C86	116(1)	C8–C81–C86	119(1)
C81–C82–C83	117(1)	C82–C83–C84	119(1)
C83–C84–C85	124(1)	C84–C85–C86	118(1)
C85–C86–C81	117(1)	C86–C81–C82	126(1)
C8–N2–N4	124.0(7)	C1–N2–N4	121.7(8)
N2–N4–C10	112.9(9)	N4–C10–C101	115(1)
C10–C101–C102	123(1)	C10–C101–C106	113(1)
C101–C102–C103	118(1)	C102–C103–C104	119(1)
C103–C104–C105	124(1)	C104–C105–C106	119(1)
C105–C106–C101	117(1)	C106–C101–C102	124(1)
Best planes			
I: C1,N1,C7,C8,N2	II: C1,C2,C4,C5,Mo	III: C7,N3,C9	IV: C81–C86
V: N2,N4,C10	VI: N4,C10,C101	VII: C101–C106	

(*continued*)

TABLE 4. (*continued*)

Interplanar angles			
I/II: 133.3(3)	I/III: 22(1)	I/IV: 3.1(5)	I/V: 155.6(8)
V/VI: 98(1)	VI/VII: 22(1)	I/VII: 55.8(5)	
Dihedral angles			
N1–C7–N3–C9	−87(1)	C1–N2–N4–C10	−137(1)
N2–N4–C10–C101	−173.7(8)	N4–C10–C101–C106	175(1)
C7–C8–C81–C82	−127(1)		

[a] E.s.d.s are given in parentheses, see Fig. 1 for atomic numbering. [b] The labeling of the hydrogen atoms follows that of the carbon atoms to which they are attached. [c] The roman numerals designate the following positions of equivalent symmetry: I: x, y, z; II: $x+0.5, -y+0.5, z+0.5$; III: $-x, -y, -z$.

quasi-3CRs with $[Cr(CN)(CO)_5]^-$. Complex **8**, for example, has thus been prepared by both the 4CC and the 3CR route, the latter using $PhCH_2N{=}CHPh$ (see 'Experimental'). Likewise, hydantoin-4-imides as well as 4-aminoimidazolin-2-ylidene complexes are obtained in high yields from aldehydes, but not from ketones. For the organometallic 4CC products this is attributed to the strong aromatizing tendency of the carbenoid heterocycle which in turn may arise from the much greater ability of the metal complex fragments as compared to oxygen for charge delocalization.

Interesting deviations from the course of the organometallic 4CCs may well result from modifications of the acid L_nMCNH which are brought about by varying the metal and the other ligands. Thus, while 4CCs starting from $NEt_4[Co(CN)_2(dmgH)_2]$ with *in situ* generation of hydrogen isocyanide give the 'normal' products [27], the 'acidic form' of dicyanocobaloxime, $H[Co(CN)_2(dmgH)_2]$, subject to the same type of 4CC, gave rise to the salt-like compound **31** which according to elemental analysis and ^1H NMR spectra contains an additional molecule of amine. Altogether, there is evidence for three NH functions whose signals disappear on addition of D_2O, and for a single isolated aliphatic proton (see 'Experimental').

The results of an X-ray structure determination of **31** are depicted in Figs. 2 and 3; pertinent bond lengths and angles are given in Table 5; for crystallographic data see Table 7. **31** consists of a purely organic amidinium-type cation and the unchanged complex anion of the starting material which are linked together by a hydrogen bond between the anilino-(N7)H7 and the cyano nitrogen N2 (Fig. 2). Further strong H bonding is expected to occur within the well-known chelate system of the anion though, in contrast to H7, the respective protons could not be located on the Fourier difference map. The same applies to the H atoms at N8 and N9 which are apparently not involved in any H bonding, however. It is also obvious that there are no intermolecular interactions with the solvent molecule (MeOH) in the crystal lattice of **31**.

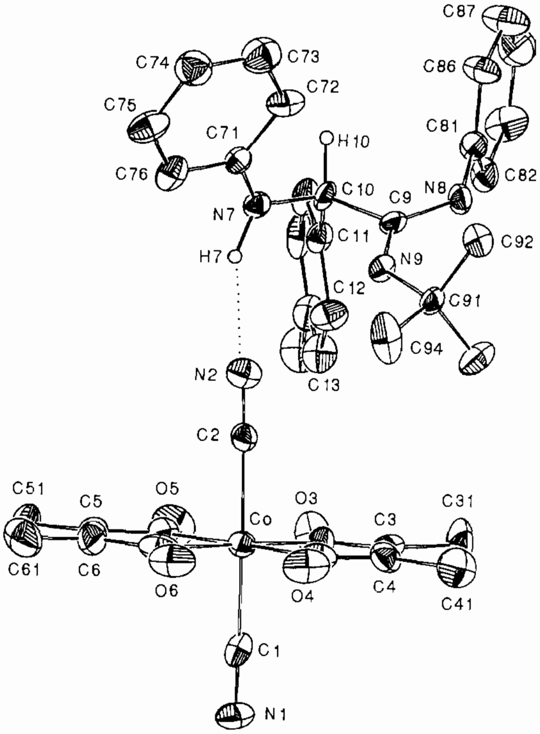
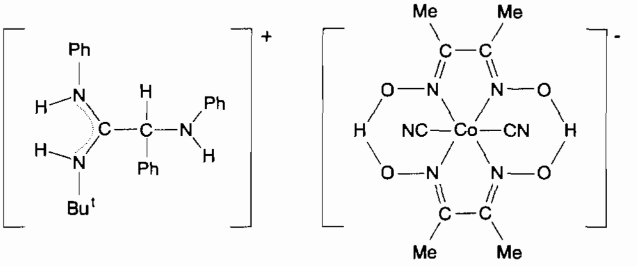


Fig. 2. ORTEP representation of the structure of **31** (thermal ellipsoids at the 30% probability level) showing the (N7)H7···N2 hydrogen bridge between the amidinium cation and the complex anion.



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Inspection of the structure of the cationic α-amino acid derivative provides some insight into the reaction course deviating from the 4CC norm. Equal C–N bond lengths, nearly 120° angles and a perfectly planar ar-

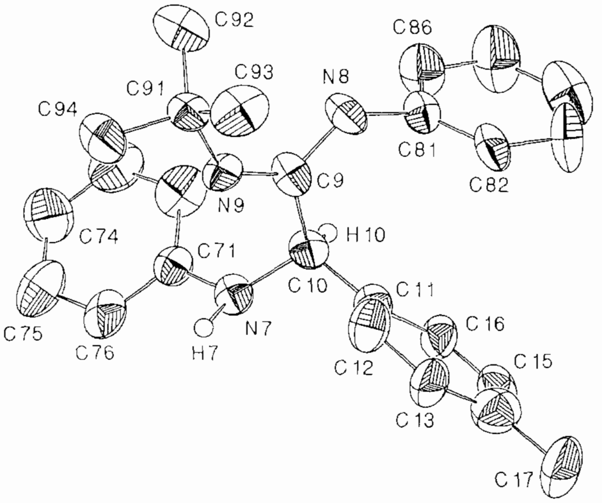


Fig. 3. ORTEP plot and labeling scheme of the amidinium cation of **31**. Thermal ellipsoids have been drawn to include 50% probability.

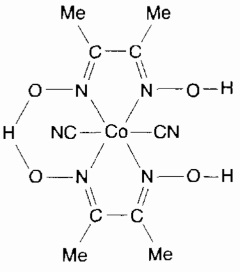
TABLE 5. Selected intermolecular contact distances, bond distances (Å), bond angles and dihedral angles (°) of **31**[a,b]

Intermolecular contact distances			
N2···N7	3.11(2)		
H7···N2	2.17(19)		
Bond distances			
Co–C1	1.886(16)	Co–N3	1.832(16)
Co–C2	1.900(16)	Co–N4	1.866(16)
C1–N1	1.160(21)	Co–N5	1.887(14)
C2–N2	1.155(22)	Co–N6	1.914(17)
C9–C10	1.352(20)	C10–N7	1.447(20)
C9–N8	1.328(20)	C10–C11	1.513(23)
C9–N9	1.310(21)	N7–C71	1.367(22)
		N8–C81	1.448(22)
		N9–C91	1.427(17)
Bond angles			
C1–Co–C2	178.6(9)	N3–Co–N4	81.5(7)
C1–Co–N3	88.9(8)	N3–Co–N5	100.0(7)
C1–Co–N4	88.5(6)	N3–Co–N6	179.4(7)
C1–Co–N5	90.9(6)	N4–Co–N5	178.3(8)
C1–Co–N6	90.6(8)	N4–Co–N6	98.0(8)
C2–Co–N3	92.4(7)	N5–Co–N6	80.3(7)
C2–Co–N4	91.8(6)		
C2–Co–N5	88.7(6)	Co–C1–N1	178.3(1.8)
C2–Co–N6	88.0(8)	Co–C2–N2	177.2(1.5)
C10–C9–N8	119.1(1.4)	C9–C10–C11	109.8(1.3)
C10–C9–N9	118.4(1.3)	N7–C10–C11	110.5(1.2)
N8–C9–N9	122.4(1.3)	C10–N7–C71	122.9(1.3)
C9–C10–N7	111.3(1.3)	C9–N8–C81	123.8(1.3)
Dihedral angles			
N9–C9–C10–N7	19(2)		
C9–C10–N7–C71	73(2)		
N8–C9–C10–C11	77(2)		

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

rangement about C9 unequivocally reflect the characteristics of a resonance-stabilized diaminocarbenium ion which is linked to a unit clearly derived from an iminium ion (Fig. 3, Table 5). The bonding parameters are in good agreement with those of 2-chloro-2-phenoxymalonylamide amidinium chloride [36]. Hence, the 4CC in question seems to have started properly by Schiff base condensation, protonation and electrophilic addition to the isocyanide to give a highly reactive nitrilium species which instead of adding to a cyano ligand, has obviously been trapped by a second molecule of amine, however. Actually, similar products have been obtained by McFarland using dimethylammonium (dimethylamine) as 'acid (anion) component' [37].

The reduced reactivity of the cyano ligands in $H[Co(CN)_2(dmgH)_2]$ can perhaps be explained by the peculiar structure of this complex acid which is not (!) that of a coordinated hydrogen isocyanide, usually an acid of mineral acid strength. Instead, one of the OHO bridges of the chelate system has been protonated to give **32** [38], presumably both, a weak acid and a weak CN nucleophile. These results clearly emphasize the importance for stoichiometric 4CCs of a proper choice of the metal complex fragment to which CNH (CN^-) is bonded. For their catalytic conductance presently under study this is even more important.



32

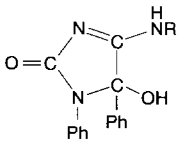
The atomic positions of the anion $[Co(CN)_2(dmgH)_2]^-$ in **31** and those of $K[Co(CN)_2(dmgH)_2] \cdot \frac{1}{2}H_2O$ are almost congruent; minor differences show up in the ranges spanned by the four Co–N distances to the chelate system though the relatively high standard deviations preclude a more profound interpretation.

5. *Detachment of the heterocycle from the complex*

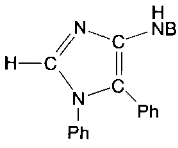
The methods of detachment from metal complexes of metal–carbon bonded ligands, particularly of strongly bonded carbenes, are not very sophisticated as yet. In general, one only has the choice between thermal or oxidative treatment both of which proceed with complete destruction of the system and often also of portions of the desired product. Oxidative cleavage of the metal–carbon bond is usually carried out under phase transfer conditions with a large excess of $KMnO_4$ in the presence of Fe^{3+} [39] or, cleaner, with Ce^{4+} to give the oxo derivative of the carbenoid ligand. The metal ends up in a high oxidation state depleted of its ligand sphere.

We have applied this method to our 3CC product complexes and obtained 4-amino-oxazolinones obviously not accessible by a direct organic route from KOCN, isocyanide and ketone. In this case, the two-step synthesis via the transition metal complex of 4-t-butylimino-5-dimethyloxazolidin-2-one, a member of a group of biologically and pharmaceutically active substances, proved superior to the organic four-step procedure [19]. In contrast, hydantoin-4-imides, expected products from the oxidative decomposition of the organometallic 4CC products described in this paper, are easily obtained according to Ugi (see above).

Though a metal-promoted synthetic approach to hydantoin-4-imides thus appeared meaningless, we wanted to be sure that nothing else happened and undertook a study of the oxidative degradation of the {1-phenyl-4-amino-5-phenylimidazoline-2-ylidene}chromium complexes **1** and **3**. To our surprise, the heterocycle isolated from the reaction of **1** in a very good yield was not identical with the organic product obtained from KOCN, CyNC, PhCHO and $PhNH_3Cl$ [40]. Instead, further oxidation had taken place which, possibly via epoxidation of the C–C double bond and hydrolysis, gave rise to 4-amino-5-*hydroxy*-Δ^3-imidazoline-2-ones **33**. Further details on the preparation and characterization of these (and related) compounds of which also an X-ray structure analysis has been carried out (**33b**) will be reported elsewhere.



(R=Cy(**33a**), Bu^t (**33b**))



34

Encouraged by these results which once more demonstrate the great possibilities brought into organic synthesis by the use of transition metals, we searched for alternative ways of removing the heterocycle from the complex. From our interest in catalytic 4CCs, it appeared particularly desirable not to destroy the complex completely, a problem which has now been solved by simple substitution. Displacement of amino carbene ligands from complexes of the type $[Cr(CO)_5\{C(R)NHR'\}]$ had earlier been achieved with pyridine [41]. Heating of **3** under reflux in n-hexane with a tenfold excess of pyridine for 18 h accordingly provides a colorless crystalline solid, **34**, in 85% yield. Both, the spectroscopic data (see 'Experimental') and an X-ray structure determination of **34** (Fig. 4) prove its identity as 1-phenyl-4-t-butylamino-5-phenylimidazole, the C2–H tautomer of the metal bonded N3–H carbene form.

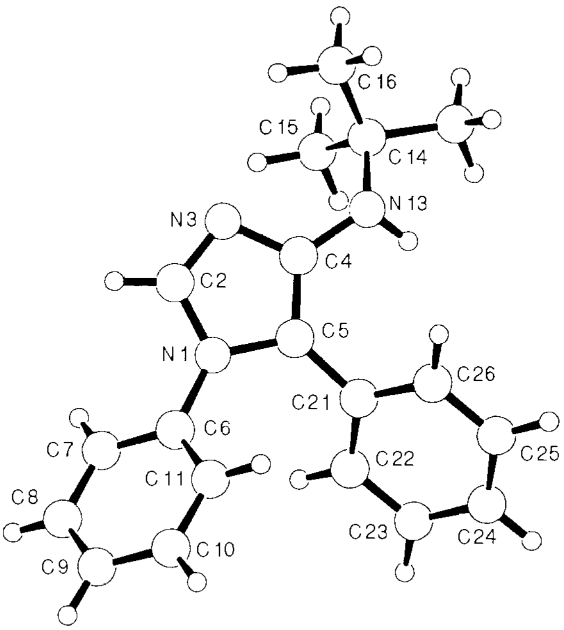


Fig. 4. Structure of **34**. Selected bond distances (Å): N1–C2 1.359(2); N1–C5 1.402(2); C2–N3 1.315(2); N3–C4 1.381(2); C4–C5 1.376(2).

Further studies of methods of ligand detachment, e.g. in the presence of carbene trapping reagents, are presently under way to benefit from the special properties of nucleophilic carbenes in transition metal complexes totally unexploited as yet.

Experimental

All operations were carried out in an inert gas atmosphere (Ar) by using Schlenk tube techniques. The solvents were deoxygenated and dried prior to use. IR 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), 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. 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) [42] and $H[Co(CN)_2(dmgH)_2]\cdot 2H_2O$ [38a] were prepared by published methods. All other reagents were purchased from Aldrich.

TABLE 6. Analytical and other data

Complex	Molecular weight (g/mol)	Melting point (dec.) (°C)	Yield (%)	Analyses (%)			
					C	H	N
1	$C_{26}H_{23}CrN_3O_5$	140	89	(calc.)	61.29	4.52	8.25
	(509.20)			(found)	61.28	4.61	8.12
2	$C_{21}H_{15}CrN_3O_5$	140	81	(calc.)	57.15	3.43	9.56
	(441.39)			(found)	56.86	3.61	9.47
3	$C_{24}H_{21}CrN_3O_5$	152	92	(calc.)	59.63	4.38	8.69
	(483.48)			(found)	59.43	4.40	8.57
4	$C_{21}H_{23}CrN_3O_5$	121	77	(calc.)	56.12	5.12	9.35
	(450.15)			(found)	56.07	5.03	9.26
5	$C_{18}H_{17}CrN_3O_5$	111	59	(calc.)	53.07	4.18	10.32
	(407.38)			(found)	53.08	4.27	10.05
6	$C_{28}H_{21}CrN_3O_5$	80	68	(calc.)	63.28	3.95	7.91
	(531.52)			(found)	63.36	4.70	7.30
7	$C_{27}H_{25}CrN_3O_6$	60	59	(calc.)	60.11	4.67	7.79
	(539.51)			(found)	60.26	5.07	7.15
8	$C_{27}H_{25}CrN_3O_5$	105	74	(calc.)	61.95	4.81	8.03
	(523.51)			(found)	61.58	5.19	8.00
9	$C_{24}H_{21}MoN_3O_5$	135	86	(calc.)	54.44	3.97	7.94
	(527.42)			(found)	54.41	3.98	7.91
10	$C_{24}H_{21}N_3O_5W$	145	76	(calc.)	46.83	3.41	6.83
	(615.33)			(found)	46.86	3.55	6.73
11	$C_{26}H_{26}N_4O_5W$	145	43	(calc.)	47.43	3.98	8.51
	(658.37)			(found)	47.21	4.21	8.06
12	$C_{24}H_{20}ClN_3O_5W$	120	98	(calc.)	44.37	3.10	6.47
	(649.74)			(found)	44.72	3.49	6.42
13	$C_{25}H_{22}CrN_4O_5$	140	83	(calc.)	58.82	4.34	10.98
	(510.47)			(found)	57.73	4.52	10.56
14	$C_{24}H_{22}CrN_4O_5$	110	41	(calc.)	57.83	4.45	11.24
	(498.46)			(found)	58.47	4.87	10.78
15	$C_{23}H_{25}CrN_3O_5S$	60	66	(calc.)	54.53	4.97	8.28
	(507.53)			(found)	54.05	4.82	7.77
16	$C_{26}H_{22}N_4O_5W$	145	69	(calc.)	61.87	4.31	8.17
	(654.34)			(found)	61.79	4.41	7.90
17	$C_{21}H_{23}N_3O_5SW$	106	95	(calc.)	41.09	3.78	6.85
	(613.35)			(found)	41.43	4.19	6.05
18	$C_{24}H_{21}N_3O_5SW$	140	79	(calc.)	44.53	3.27	6.49
	(647.36)			(found)	45.22	3.87	6.73
19	$C_{42}H_{36}Cr_2N_6O_{10}$	> 250	63	(calc.)	56.76	4.05	9.46
	(888.84)			(found)	56.80	4.13	9.48
20	$C_{38}H_{36}Cr_2N_6O_{10}$	71	70	(calc.)	54.29	4.29	10.00
	(840.80)			(found)	54.26	4.64	9.13
21	$C_{53}H_{44}Cr_2N_6O_{10}$	210	66	(calc.)	61.87	4.31	8.17
	(1028.96)			(found)	61.79	4.41	7.90
22	$C_{38}H_{32}N_6O_{12}W_2$	180	72	(calc.)	40.31	2.85	7.42
	(1132.40)			(found)	39.80	3.41	7.73
23	$C_{46}H_{40}N_6O_{10}W_2$	152	63	(calc.)	45.85	3.35	6.98
	(1204.56)			(found)	45.08	3.49	6.62
24	$C_{43}H_{42}Cr_2N_6O_{10}$	100	83	(calc.)	56.95	4.67	9.27
	(906.88)			(found)	56.60	4.69	9.08
25	$C_{25}H_{22}CrN_4O_5$	130	61	(calc.)	58.82	4.31	10.98
	(510.09)			(found)	58.51	4.41	10.91
26	$C_{19}H_{26}CrN_4O_5$	65	39	(calc.)	51.58	5.88	12.67
	(442.13)			(found)	51.51	5.58	12.68
27	$C_{17}H_{22}CrN_4O_5$	60	39	(calc.)	49.28	5.31	13.52
	(414.09)			(found)	49.30	5.54	12.87
28	$C_{25}H_{22}MoN_4O_5$	120	35	(calc.)	53.95	3.96	10.07
	(556.06)			(found)	53.64	4.11	9.97

TABLE 7. Crystallographic data collection parameters

	28	**31**
Crystal data		
Formula	$C_{25}H_{23}MoN_4O_5$	$C_{35}H_{44}CoN_9O_4 \cdot CH_3OH$
Molecular weight (g/mol)	555.42	745.31
Crystal size (mm)	0.44 × 0.32 × 0.26	0.25 × 0.42 × 0.29
Crystal system	mononclinic	monoclinic
Space group	$P2_1/n$	$P2_1$
Cell parameters		
a (Å)	12.674(3)	8.464(2)
b (Å)	12.078(5)	19.168(7)
c (Å)	17.362(3)	12.771(3)
β (°)	91.30(2)	98.73(2)
U (Å^3)	2657.1	2048
Z	4	2
D_c (g/cm^3)	1.392	1.209
Collection and refinement parameters		
Radiation (λ (Å))	graphite-monochromated Mo Kα (0.71069)	
μ (cm^{-1})	5.29	4.85
Temperature (K)	293	293
Scan mode	ω-scan	ω-scan
2θ Limits (°)	$4 \leqslant 2\theta \leqslant 50$	$4 \leqslant 2\theta \leqslant 50$
Total no. reflections	3926	3890
No. data	2633 ($I \geqslant 2\sigma(I)$)	2478 ($I \geqslant 3\sigma(I)$)
No. parameters	316	467
R	0.093	0.080
R_w	0.054	0.080
Programs used	SHELXS-86, XTAL 2.2, ORTEP	SHELXS-86, XTAL 3.0, DIFABS, ORTEP

General procedure for the preparation of the pentacarbonyl{4-amino-Δ^4-imidazolin-2-ylidene}chromium, -molybdenum and -tungsten complexes 1–24

To a stirred solution of 1.40 mmol of $NEt_4[M(CN)(CO)_5]$ (M = Cr, Mo, W) in 20 ml of MeOH were added 1.40 mmol of aldehyde via syringe followed by 1.40 mmol of isocyanide at ice-bath temperature. To this solution 1.40 mmol of amine hydrochloride in 20 ml of MeOH were added dropwise. Usually a sudden color change occurred to deep yellow or orange. 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 n-pentane/diethyl ether (1:1). The colorless to yellow products were recrystallized from dichloromethane/pentane.

Complexes **13** and **14** were isolated directly by filtration of the primary reaction mixture and recrystallization from diethyl ether/pentane.

For the isolation of the complexes **11**, **12**, **18**, **22** and **23**, the reaction mixture was taken to dryness and extracted with $CHCl_3$. The extracts were dried with Na_2SO_4, filtered and again evaporated to dryness to give analytically pure products. For spectroscopic data see Table 1–3, for elemental analyses and physical properties, see Table 6.

Preparation of pentacarbonyl{1-benzyl-4-cyclohexylamino-5-phenyl-Δ^4-imidazolin-2-ylidene}chromium (8) via three-component cycloaddition

0.15 g (1.40 mmol) of cyclohexylisocyanide was added to a solution of 0.48 g (1.40 mmol) of $NEt_4[Cr(CN)(CO)_5]$, 0.27 g (1.40 mmol) of *N*-benzylidene benzimine and 0.19 ml (1.40 mmol) of HBF_4 (etheral solution, 54%) in 20 ml of CH_2Cl_2 at 0 °C. The yellow reaction mixture was allowed to stir for 24 h at room temperature. Addition of silica gel, evaporation of the solvent and chromatographic work-up (petroleum ether/ether (1:1); chromatography column (2 × 20 cm) charged with silica gel) resulted in 0.54 g (74%) of **8**.

General procedure for the preparation of the pentacarbonyl{1-(N-imino)-4-t-butylamino-Δ^4-imidazolin-2-ylidene}chromium and -molybdenum complexes 25–28

1.44 mmol of $NEt_4[M(CN)(CO)_5]$ (M = Cr, Mo), 2.88 mmol of aldehyde and 0.16 ml (1.44 mmol) of t-butylisocyanide were dissolved in 10 ml of MeOH at ice-bath temperature. To this solution was added 0.15 g (1.44 mmol) of hydrazinium dichloride. After reacting

TABLE 8. Fractional atomic coordinates and thermal parameters (×100 Å^2) of the non-hydrogen atoms of **28**[a]

Atom	x/a	y/b	z/c	U_{eq}[b]
Mo	0.12357(6)	0.16075(7)	0.771739(6)	3.70(3)
O2	0.0756(7)	−0.0122(9)	0.5864(6)	13.9(6)
O3	0.3155(8)	0.2515(9)	0.6255(7)	14.1(6)
O4	0.2682(6)	−0.0134(7)	0.8009(6)	11.6(5)
O5	0.1840(8)	0.3293(8)	0.8490(6)	12.1(5)
O6	−0.0646(7)	0.0677(9)	0.8154(6)	11.6(5)
N1	0.0346(7)	0.3873(7)	0.6418(5)	5.3(4)
N2	0.0827(6)	0.7344(6)	0.3676(5)	4.3(3)
N3	0.0464(6)	0.4520(7)	0.4264(6)	5.9(4)
N4	0.1389(6)	0.8359(7)	0.3556(5)	5.3(4)
C1	0.0155(8)	0.2816(9)	0.6614(7)	5.0(5)
C2	0.094(1)	0.054(1)	0.637(1)	9.7(8)
C3	0.243(1)	0.218(1)	0.6616(8)	9.0(7)
C4	0.2136(8)	0.054(1)	0.7691(8)	6.9(6)
C5	0.158(1)	0.268(1)	0.7995(8)	7.7(7)
C6	0.0020(9)	0.104(1)	0.7771(9)	8.2(6)
C7	0.0515(8)	0.5604(9)	0.3971(7)	4.9(5)
C8	0.1283(7)	0.6388(8)	0.4015(6)	5.1(5)
C9	0.071(1)	0.3564(9)	0.3724(8)	8.0(6)
C10	0.1871(8)	0.8723(8)	0.4184(7)	5.2(5)
C81	0.2391(8)	0.6337(8)	0.4325(8)	5.4(5)
C82	0.1790(8)	0.172(1)	0.1201(7)	6.8(5)
C83	0.0728(9)	0.172(1)	0.091(1)	9.2(7)
C84	0.051(1)	0.128(1)	0.016(1)	9.0(8)
C85	0.132(1)	0.089(1)	0.9643(9)	9.9(7)
C86	0.257(1)	0.5915(9)	0.5078(8)	8.0(6)
C91	0.008(1)	0.648(1)	0.6965(9)	16.2(9)
C92	0.185(1)	0.368(1)	0.3460(9)	12.4(8)
C93	0.067(1)	0.2567(9)	0.4293(9)	13.3(8)
C101	0.2438(7)	0.4713(9)	0.0921(8)	4.7(5)
C102	0.2335(8)	0.527(1)	0.1641(7)	6.3(6)
C103	0.158(1)	0.612(1)	0.1681(8)	7.8(6)
C104	0.099(1)	0.641(1)	0.1010(9)	8.5(7)
C105	0.112(1)	0.591(1)	0.030(1)	8.9(7)
C106	0.1873(9)	0.502(1)	0.0237(8)	7.4(6)

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

for 2 h and warming up to room temperature, silica gel was added, and the mixture evaporated to dryness. The resulting powder was transferred to a chromatography column charged with silica gel (2×15 cm) and eluted with petroleum ether/diethyl ether (1:1). The first colorless fraction was concentrated to about 10 ml. Cooling of this solution to −78 °C resulted in colorless, very air-sensitive crystals of **25**–**28**.

During chromatographic work-up of **26**, a second band separated. The solution was evaporated to dryness and the solid recrystallized from CH_2Cl_2/petroleum ether (1:1) resulting in **29**.

TABLE 9. Fractional atomic coordinates and thermal parameters (Å^2) of the non-hydrogen atoms of **31**[a]

Atom	x/a	y/b	z/c	U_{eq}[b]
Co	0.5873(3)	0.5018(3)	0.0467(2)	0.0404(6)
C1	0.652(2)	0.510(1)	−0.088(1)	0.044(5)
N1	0.691(2)	0.514(1)	−0.171(1)	0.067(7)
C2	0.519(2)	0.491(1)	0.181(1)	0.044(6)
N2	0.473(2)	0.4868(9)	0.261(1)	0.062(7)
N3	0.664(2)	0.5899(8)	0.079(1)	0.049(5)
N4	0.797(2)	0.4783(9)	0.102(1)	0.056(6)
N5	0.374(2)	0.5231(2)	−0.012(1)	0.053(6)
N6	0.0509(2)	0.4097(8)	0.012(1)	0.060(6)
O3	0.571(2)	0.6466(8)	0.060(1)	0.068(6)
O4	0.852(2)	0.4120(8)	0.106(1)	0.076(7)
O5	0.320(2)	0.586(1)	−0.019(1)	0.083(7)
O6	0.613(2)	0.3537(9)	0.029(1)	0.081(7)
C3	0.812(3)	0.595(1)	0.123(2)	0.061(8)
C4	0.891(2)	0.528(1)	0.135(1)	0.056(7)
C5	0.277(2)	0.470(1)	−0.043(1)	0.069(9)
C6	0.358(3)	0.404(1)	−0.028(2)	0.068(9)
C31	0.891(3)	0.666(1)	0.156(2)	0.11(1)
C41	1.068(2)	0.522(2)	0.182(2)	0.09(1)
C51	0.113(2)	0.477(1)	−0.92(2)	0.09(1)
C61	0.281(3)	0.335(1)	−0.056(2)	0.10(1)
C9	0.577(2)	0.5859(9)	0.525(1)	0.042(6)
C10	0.395(2)	0.5923(9)	0.501(1)	0.041(6)
N7	0.322(1)	0.5275(8)	0.461(1)	0.041(5)
N8	0.660(2)	0.6312(8)	0.591(1)	0.049(5)
N9	0.646(1)	0.5349(7)	0.481(1)	0.041(4)
C11	0.349(2)	0.6511(9)	0.424(1)	0.045(6)
C12	0.422(2)	0.661(1)	0.333(2)	0.060(7)
C13	0.367(2)	0.715(1)	0.258(2)	0.063(8)
C14	0.256(2)	0.763(1)	0.280(2)	0.065(8)
C15	0.185(2)	0.752(1)	0.370(2)	0.071(8)
C16	0.230(2)	0.6982(9)	0.443(1)	0.052(6)
C17	0.201(3)	0.822(1)	0.207(2)	0.09(1)
C71	0.311(2)	0.4703(9)	0.523(1)	0.040(6)
C72	0.373(2)	0.470(1)	0.629(1)	0.062(7)
C73	0.353(2)	0.408(1)	0.690(2)	0.075(9)
C74	0.276(3)	0.350(1)	0.644(2)	0.073(9)
C75	0.220(2)	0.350(1)	0.539(2)	0.067(8)
C76	0.238(2)	0.412(1)	0.477(2)	0.058(7)
C81	0.586(2)	0.6861(9)	0.645(1)	0.045(6)
C82	0.561(2)	0.7494(9)	0.594(1)	0.055(7)
C83	0.507(3)	0.804(1)	0.652(2)	0.077(9)
C84	0.484(3)	0.793(1)	0.755(2)	0.09(1)
C85	0.511(3)	0.730(1)	0.803(2)	0.09(1)
C86	0.559(3)	0.675(1)	0.747(1)	0.064(8)
C91	0.810(2)	0.515(1)	0.490(1)	0.043(6)
C92	0.883(2)	0.501(2)	0.605(1)	0.069(7)
C93	0.896(2)	0.568(1)	0.435(2)	0.071(8)
C94	0.812(2)	0.447(1)	0.434(2)	0.09(1)
O80	0.933(1)	0.2116(7)	0.262(1)	0.067(5)
C80	1.023(3)	0.183(1)	0.340(2)	0.11(1)

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

Alternative preparation of pentacarbonyl(4-t-butylamino-5-isopropyl-Δ^3-oxazolin-2-ylidene)chromium (29)

To a solution of 0.50 g (1.44 mmol) of $NEt_4[Cr(CN)(CO)_5]$ in 10 ml of isobutyraldehyde were added 0.20 ml (1.44 mmol) of HBF_4 (etheral solution, 54%) and 0.16 ml (1.44 mmol) of t-butylisocyanide at 0 °C. The yellow mixture was stirred for 12 h and allowed to warm up to room temperature. Addition of silica gel and evaporation to dryness resulted in a powder which was transferred to a column charged with silica gel (2×15 cm) and eluted with petroleum ether/ether (1:1). The yellow fraction was concentrated and recrystallized from CH_2Cl_2/petroleum ether (1:1) to give 0.18 g (33%) of **29**. M.p. 128 °C (dec.). *Anal.* Calc. for $C_{15}H_{18}CrN_2O_6$ (374.35 g/mol): C, 48.13; H, 4.81; N, 7.49. Found: C, 48.19; H, 5.05; N, 7.52%. ^1H NMR (δ, DMSO-d_6): 0.52 (d, Me, 3H); 1.16 (d, Me, 3H); 1.48 (s, Bu^t, 9H); 2.30 (m, $C\mathit{H}Me_2$, 1H); 5.12 (d, $C\mathit{H}(Pr^i)$, 1H); 9.68 (s, NH, 1H). ^{13}C NMR (δ, DMSO-d_6): 13.1 (Me); 19.5 (Me); 27.7 (Bu^t); 31.1 (CH); 55.0 ($\mathit{C}Me_3$); 88.6 ($\mathit{C}(Pr^i)$); 178.1 (CN); 218.1 (CO_{eq}); 223.6 (CO_{ax}); 272.9 (C-carbene). IR (KBr, cm^{-1}): 3360s ν(NH), 2967s, 2920s, 2877s ν(CH), 2060m, 1979vs ν(CO), 1615s, 1512m ν(heterocycle).

Preparation of 31

To a stirred solution of 1.0 g (2.6 mmol) of $H[Co(CN)_2(dmgH)_2]\cdot 2H_2O$ in 20 ml of MeOH were added 0.24 g (2.6 mmol) of aniline and 0.31 g (2.6 mmol) of *p*-methylbenzaldehyde followed by 0.21 g (2.6 mmol) of t-butylisocyanide. After 12 h, the mixture was concentrated to about half of the original volume and allowed to stand at room temperature overnight which resulted in 0.21 g (11%) of **31** as orange crystals. M.p. 112–115 °C (dec.). *Anal.* Calc. for $C_{36}H_{48}CoN_9O_5$ (745.31 g/mol): C, 57.96; H, 6.49; N, 16.91. Found: C, 56.85; H, 6.06; N, 16.60%. ^1H NMR (δ, DMSO-d_6): 1.50 (s, Bu^t, 9H); 2.20 (s, Me (dmgH), 12H); 2.35 (s, Me (Tol^p), 3H); 5.20 (s, CH, 1H); 6.25 (s, NH, 1H); 6.70–7.65 (m, Ph + Tol^p, 14H); 8.65 (s, NH, 1H); 10.50 (s, NH, 1H). IR (KBr, cm^{-1}): 3342w, 3245m ν(NH), 2128s ν(CN), 1633s, 1602s, 1588s, 1507s (amidinium).

Preparation of 1-N-phenyl-4-t-butylamino-5-phenylimidazole (34)

To a stirred suspension of 0.97 g (2.0 mmol) of **3** in 20 ml of hexane were added 2 ml of pyridine (25.2 mmol) and the mixture was heated at reflux for 18 h. Filtration of the yellow solution, evaporation to dryness and recrystallization from THF/pentane resulted in the colorless product (0.49 g, 85%). M.p. 95 °C. *Anal.* Calc. for $C_{19}H_{21}N_3$ (291.39 g/mol): C, 78.32; H, 7.26; N, 14.42. Found: C, 74.53; H, 7.24; N, 12.90%. ^1H NMR (δ, DMSO-d_6): 7.60 (s, CH, 1H); 7.40–7.00 (m, Ph, 10H); 3.82 (s, NH, 1H); 1.20 (s, Bu^t, 9H). ^{13}C NMR (δ, DMSO-d_6): 145.2 (C2); 136.8 (C4); 134.7–124.6 (aromatic C); 114.5 (C-Ph); 51.7 (CH); 30.0 ($C(\mathit{C}H_3)_3$). IR (KBr, cm^{-1}): 3227 m ν(NH), 1709m ν(C=N), 1600s ν(C=C). MS (EI), *m/z* (rel. int. (%)): 291 (78), (M^+); 276 (68), ($M^+ - Me$); 235 (100), ($M^+ - C_4H_8$).

X-ray structure determinations

Single crystals of **28** were grown by cooling a saturated solution in petroleum ether/ether (1:1), those of **31** from a concentrated solution in MeOH. Crystals of suitable size were mounted in glass capillaries. All crystallographic data were collected at 293 K on a STOE four circle-diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Unit cell parameters were obtained by a least-squares refinement of the angular settings from 20 reflections, well distributed in reciprocal space and lying in a 2θ range of 10–25°. Crystallographic data are given in Table 7.

All data were corrected for Lorentz–polarization effects during the final stages of data reduction. An absorption correction was carried out for **31**. The structures were solved by employing a combination of direct methods and difference Fourier techniques with scattering factors for neutral atoms taken from the literature [43]. Calculations were carried out on a VAX computer using the programs SHELXS-86 [44], XTAL 2.2/3.0 [45], DIFABS [46] and ORTEP [47]. After the non-hydrogen atoms were located and refined (Tables 8 and 9), the hydrogen atoms of **28** were placed in positions suggested by the difference Fourier maps. In the structure of **31**, the hydrogen atoms H7 and H10 were placed in calculated positions. Final refinements included anisotropic thermal parameters for all non-hydrogen atoms and isotropic ones for the hydrogen atoms. The full-matrix least-square refinements were based on *F*, and the function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$. Agreement factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma(w||F_o| - |F_c||^2)/\Sigma(w|F_o|^2)]^{1/2}$, $w = 1/\{\sigma(F_o)\}^2$.

Supplementary material

Tables of anisotropic thermal parameters for the non-hydrogen atoms (Tables 10 and 11) and hydrogen positional and thermal parameters (Tables 12 and 13), and listings of observed and calculated structure factors for all observed reflections are available from the authors on request.

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