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Reactions at the coordinated trichloromethyl isocyanide. Part VII. α-Chloroalkenylisocyanide versus oxazolin-2-ylidene(ato) complex formation ☆

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Dedicated to Professor Wolfgang Beck on the occasion of his 75th birthday.

Abstract

Under aprotic conditions, $Cr(CO)_5CNCCl_3$ (**1**) reacts with triphenylphosphine in the presence of aromatic aldehydes or ketones to give the α-chloroalkenylisocyanide complexes *cis*(*Z*)- and *trans*(*E*)-$Cr(CO)_5CNCCl{=}CRR'$ {R = H, R′ = 4-C_6H_4F (**7**), 4-C_6H_4-$CH{=}C(Cl)NCCr(CO)_5$ (**8**)} and $Cr(CO)_5CNCCl{=}CR_2$ {CR_2 = fluorenylidene (**9**)}. Two further representatives of this class of compounds, $Cr(CO)_5CNCCl{=}CCl_2$ (**10**) and $Cr(CO)_5CN{-}CCl{=}CCl{-}NCCr(CO)_5$ (**11**), have been obtained in low yields by reduction of **1** with zinc. Reactions with pyrrolidine of the isomeric mixtures **7** and **8** afford the alkylideneamino(pyrrolidino)carbene complexes **13** and **14**. An X-ray study of **13** shows the two π-systems within the amino(imino)carbene ligand to be approximately orthogonal to one another. With tris(dimethylamino)phosphine in the place of triphenylphosphine, complex **1**, 9-fluorenone plus a secondary amine combine to the 4-amino-Δ^3-oxazolin-2-ylidene chromium complexes **17** and **19**, the latter of which has been protonated, alkylated and subject to an X-ray structure analysis. Reasons for the different modes of reaction in the system **1**/PR_3/RR′C=O are discussed and compared with the "dependence on the metal" of reactions in the system $L_nMCN{-}CH{-}PPh_3$/RR′C=O {$L_nM = (OC)_5Cr$, $(OC)_5W$ versus $Cl(Ph_3P)_2Pt^+$}.

Keywords: Chromium complexes; Functional Isocyanides; Carbene ligands; Organometallic Wittig reactions; Organometallic [3+2] cycloadditions; X-ray structures

1. Introduction

In a series of papers we have dealt with the chemistry of pentacarbonyl(trichloromethyl isocyanide)chromium (**1**) which due to the presence of two mutually reinforcing electrophilic centers, the unsaturated isocyano unit and the perchlorinated α-C atom, possesses an extremely high synthetic potential [1–7]. Although most reactions occur at the two electrophilic centers C^1 and C^3 jointly, affording a broad palette of carbene, C-heterocycle, and isocyanide complexes, it is possible, in some cases, to limit the reaction to the trichloromethyl group of **1** and thereby obtain new functional isocyanides.

To the latter category also belong the reactions with phosphines as nucleophiles which have turned out to be a true bonanza for versatile organometallic/organophosphorus

☆ For Part VI, see Ref. [7].

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[1] X-ray structure determinations.

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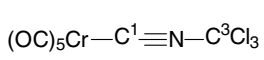
synthons and syntheses such as the combined isocyano-Wittig/metallo-nitrile-ylid reagent **2** with its carbonyl-(isocyano)methyleneation and [3+2] cycloaddition reaction patterns [6,8,9].



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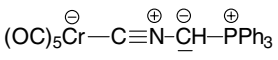

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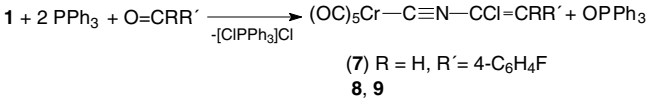
In an earlier report, we have demonstrated that the reaction scheme established by Appel and co-workers for the two component-system CCl_4/PPh_3 can be applied point by point to exactly predict what kind of chemistry is going on in the combination **1**/PPh_3 [6,10]. If we simply replace a covalently bonded chlorine atom in Appel's scheme by the electronically similar pentacarbonyl(cyano)chromium radical we end up with a series of *P*-functionalized isocyanide complexes of which **4**, **5** (as triethylphosphonium derivative) and **6** have already been isolated and characterized (Scheme 1) [6].

Only **3** has so far eluded isolation though in view of the general validity of Scheme 1 there is little room for doubt about its intermediacy. Further evidence for the existence of **3** now comes from its trapping in Wittig-type reactions with carbonyl compounds on which we report in the following. The classical analogue is the three-component system $CCl_4/PPh_3/O{=}CHPh$ used by Rabinowitz and Marcus for the preparation of dichlorostyrene ($Cl_2C{=}CHPh$) [11]. Furthermore, we show that replacing triphenylphosphine by tris(dimethylamino)phosphine alters the mechanism in a central point: now the metallo-nitrile-ylid nature of **3** or its $P(NMe_2)_3$ derivative, respectively, comes to the fore resulting in [3+2] cycloadditions with ketones to give chromium–C bonded oxazoli(di)nes.

2. Results and discussion

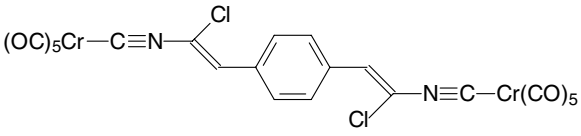
2.1. One-step syntheses of α-chloroalkenylisocyanide complexes from $Cr(CO)_5CNCCl_3$

Addition at room temperature of two equivalents of triphenylphosphine to a 1:1 mixture of **1** and the respective carbonyl compound in diethylether – in the case of the dialdehyde a 4:2:1-stoichiometry was chosen – resulted in a change of colour from yellow to orange and an immediate precipitation of chlorotriphenylphosphonium chloride (Eq. (1)). Strictly aprotic conditions were maintained during work-up which included chromatography on silica and finally led to the α-chloroalkenylisocyanide complexes as microcrystalline yellow (**7**), orange (**8**) or light green materials (**9**) in good yields (Section 3).



(**7**) R = H, R′ = 4-C_6H_4F
8, **9**

(1)



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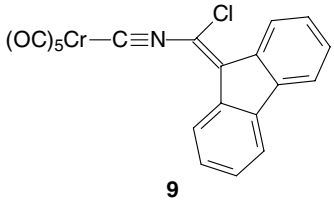

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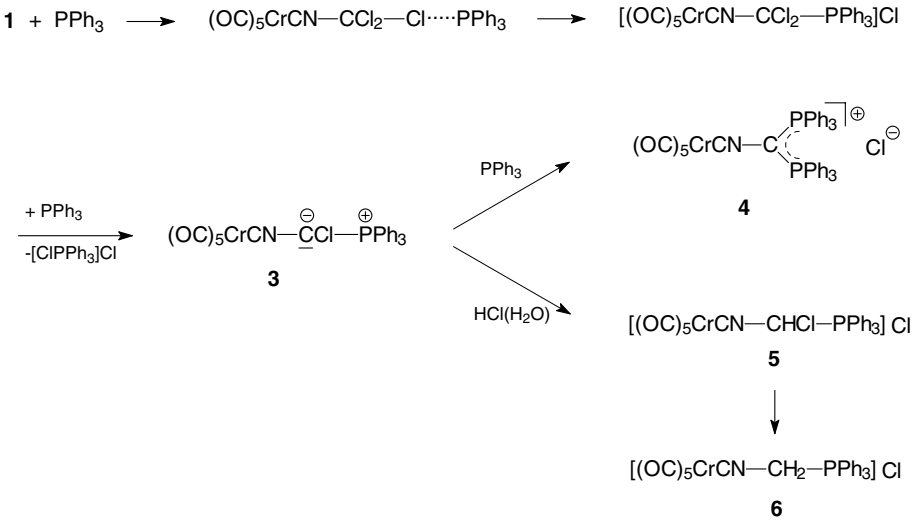


Scheme 1.

As indicated by the ^{1}H and ^{13}C NMR spectra, complexes **7** and **8** form mixtures of *cis*(*Z*)- and *trans*(*E*)-isomers which have so far evaded separation. In fact, the ^{1}H NMR spectra clearly show **7** to consist of two, and **8** to consist of the expected three stereoisomers. This is gathered from the vinylic protons which in the case of **7** give rise to two singlets at δ 6.80 and 6.51 having an intensity ratio of 1:2.5, while complex **8** exhibits resonances at δ 7.18, 6.75 and 6.49 of relative intensities 1:2:2. Assignments of signals to a given isomer were not possible, however. In the ^{13}C NMR spectra, it is particularly the carbonyl- and isocyanide-carbon signals of the pentacarbonyl(isocyanide)chromium entity of **7** and **8** which appear doubled in number. Some doubling of signals also occurs for the alkenyl carbon atoms (Table 2), while there is no indication in the ^{13}C NMR of **8** of a third isomer. Only one set of signals, naturally, is found for compound **9**.

The generally small differences in the chemical shifts of the *axial*- and *equatorial*-CO carbon atoms of the pentacarbonylchromium group of <2 ppm point to marked acceptor properties of the new ligands [12], an interpretation which is supported by the positions at particularly low fields of the isocyanide-carbon resonances. A range of δ values of 110–115 for the chloro(isocyano)alkenyl carbon (>C=*C*(Cl)NC–) agrees with earlier findings and is obviously typical for this structural element [13].

The only IR bands worth mentioning are those of the CN stretching vibration which due to the enhanced π-acceptor abilities of these functional isocyanides appear at comparatively low wave numbers, and those of the *ν*(CO)-*E* mode which, consistent with bond theory, have been shifted to higher frequencies (Table 1).

The highest lines in the mass spectra (EI) correspond with the calculated molecular masses, and the parent peaks of **7** and **9** as usually with $CrCNR^{+}$ fragments devoid of the carbonyl envelope (Table 3). No evidence is found in the mass spectra for any elimination of HCl from the α-chloroalkenyl ligands of **7** or **8** to give the much sought-after isocyanoacetylenes [14,15].

Another approach to α-chloroalkenylisocyanide complexes, e.g., *cis*(*Z*)- and *trans*(*E*)-$Cr(CO)_5CN–CCl{=}CHCl$ or $Cr(CO)_5CN–CCl{=}CH_2$, consists in the elimination with zinc in glacial acetic acid of chlorine from tri- and tetrachloroethylisocyanide(pentacarbonyl)-chromium, respectively [13]. Two further representatives of this class of compounds, viz. $Cr(CO)_5CN–CCl{=}CCl_2$ (**10**) and *trans*-$Cr(CO)_5CN–CCl{=}CCl\text{-}NCCr(CO)_5$ (**11**), had very surprisingly been obtained by reduction of **1** with zinc in aprotic media; here presumably the reaction proceeds via the C^3–C^3-coupled intermediate $Cr(CO)_5CN–CCl_2–CCl_2–NCCr(CO)_5$ from which again chlorine is removed to give **11** while formation of **10** requires elimination of $Cr(CO)_5CNH$ from its partially reduced form [2]. From the IR and Raman spectra of **11** – in particular the mutually exclusive activites of the *ν*(C=C) and *ν*(CCl) – a centrosymmetric structure (overall symmetry C_{2h}) can be inferred which obviously also accounts for the unusual *ν*(CO) IR pattern ($1A_u + 4B_u$) (Table 1).

2.2. Reactions of the α-chloroalkenylisocyanide complexes 7 and 8 with pyrrolidine; X-ray structure of product 13

α-Chlorinated alkylisocyanides coordinated to pentacarbonylchromium are known to be highly prone to nucleophilic attack by amines. The absolute record holder in this respect is the trichloromethylisocyanide ligand in **1** which consumes up to seven (!) molecules of N-nucleophile resulting in diaminocarbene complex and free guanidine moieties along with three equivalents of ammonium chloride [2–4]. Though markedly less electrophilic, the parent compound of the α-chloroalkenylisocyanide complexes, $Cr(CO)_5CN–CCl{=}CH_2$, still takes up two molecules of a secondary amine HNR_2 to give the imino(amino)carbene-chromium species **12a** [16].

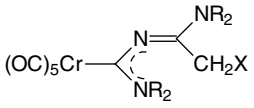
Reactions in diethylether of **7** with three and of **8** with six equivalents of pyrrolidine, by analogy, proceed smoothly following the same addition–elimination mechanism with migration of the double bond and formation

Table 1
Selected IR data (cm^{-1}) (KBr)

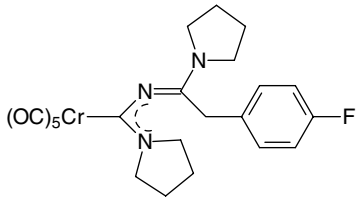
Complex	*ν*(CN)	*ν*(CO)	Others
7	2122 s	2038 s, 2000 s, sh, 1978 vs, br, 1935 s, br	1597 m *ν*(C=C)
8	2116 s	2034 s, 2006 s, sh, 1975 vs, br, 1934 s, br	1605 m *ν*(C=C)
9	2114 s	2044 s, 2007 s, sh, 1983 vs, br, 1942 s, br	1614 m *ν*(C=C)
10[a]	2118 w	2019 m, 1978 vs, 1949 m	1575 w *ν*(C=C), 823 s *ν*(CCl)
11[b,c]	2119 w	2059 s, 2019 sh, 2005 sh, 1999 s, 1953 vs	837 m *ν*(CCl)
13		2045 s, 1912 vs, br, 1888 s	1626 s *ν*(C=N), 1408 s *ν*(N=C=N)
14		2048 s, 1904 vs, br, 1875 s	1624 s *ν*(C=N), 1415 s *ν*(N=C=N)
17		2057 s, 1985 s, 1970 vs, br, 1899 s	1644 s *ν*(C=N), 1442 s *ν*(N=C=O)
19		2057 s, 1960 vs, 1923 vs, br	1638 s *ν*(C=N), 1451 s *ν*(N=C=O)
20		2072 s, 1997 m, 1927 vs, br	3206 s, br *ν*(NH), 1626 s *ν*(C=N), 1452 s *ν*(N=C=O), 1083 s, br *ν*(BF_4)
21		2071 s, 1998 s, 1934 vs, br	1665 m *ν*(C=N), 1453 s *ν*(N=C=O), 1060 s, br *ν*(BF_4)
22	2217 s		1060 vs *ν*(BF_4)
23			1523 s ν_{as}(N=C=O) + ν_{as}(NO_2), 1347 s ν_s(NO_2), 1082, 1034 vs *ν*(BF_4)

[a] In *n*-pentane.
[b] Nujol mull.
[c] Raman data of **11**: 2114 w *ν*(CN), 2049 m, 2003 s, 1956 m *ν*(CO), 1592 vs *ν*(C=C).

of the yellow crystalline substances **13** and **14** in which base functions reside in the C^1 and C^3 positions. In the infrared, accordingly, the ν(CN) bands at about 2120 cm^{-1} have disappeared in favour of two strong absorptions at 1625 and 1410 cm^{-1} which are assigned to the C=N stretching vibration of the alkylideneamino group and the ν(N---C---N) mode of the *N*,*N*′-carbene, respectively. The ν(CO)-*E* bands of the starting materials **7** and **8** experience a huge drop of some 70 wavenumbers which dramatically reflects the change from a predominant acceptor ligand, the α-chloroalkenylisocyanide, to a strong donor, the amino(imino)carbene (Table 1).



(**12a**) X = H
(**12b**) X = Cl



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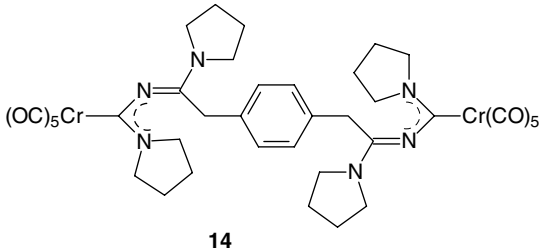
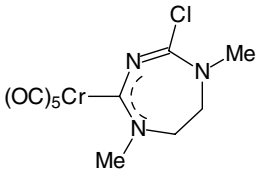


14

The NMR spectra (Table 2) show unique sets of signals, i.e., the mixtures of two or, respectively, three stereoisomers (**7**, **8**) have obviously been converted by these reactions into single complex individuals. Their ^{1}H NMR data closely resemble those of **12a** and, particularly, **12b** which have thoroughly been analyzed including their dynamics [16–18]. Only a short résumé will therefore be given here: causal for the observation of only one species each is a fast inversion at the imino nitrogen which exchanges the *cis* and *trans* positions with respect to the CN double bond; this kind of dynamics, however, is unable to equilibrate the methylene hydrogens (CH_2Ar) which due to the lack of a mirror plane – the π-systems of the two carbene substituents are perpendicular to each other – give rise to doublets of doublets, i.e., turn out diastereotopic (Table 2). Only coplanarity of the whole ligand or a rapid rotation about the C(carbene)–N(imine) bond providing temporary coplanarity, respectively, would remove the so-called 'conformational chirality'. Yet both possibilities are excluded for steric (and electronic) reasons.

Quite a number of X-ray structures of alkylideneaminocarbene complexes is meanwhile available which unanimously display approximately orthogonal arrangements of π-systems within the amino(imino)carbene ligand as the most prominent stereochemical peculiarity [19]. Thus, in the molecular structure of **13** (Fig. 1) an interplanar angle of 81.4(2)° has been determined between the carbene plane defined by the atoms N1, C6 and N3, and the alkylideneamino unit (N1, C7, C8) which solely serves the purpose of orientating the "lone pair" on the imino nitrogen in such a way that it interacts best with the empty p_z-orbital on the carbene carbon atom. Most of the remaining stereochemical features in the structure of **13** are more or less mere consequences of this carbene stabilizing measure:

- The long chromium to carbene carbon distance of 2.138(3) Å which equals that in complex $Cr(CO)_5${C(NMe$_2$)N=C(OMe)Ph} (d(Cr–$C_{carbene}$) = 2.135(4) Å) [20], yet exceeds by far that in **15** (d(Cr–$C_{carbene}$) = 2.114(3) Å) [2] or in **16** (d(Cr–$C_{carbene}$) = 2.115(2) Å) [7]; clearly, in the latter two cases the metal has to contribute significantly to the overall stabilization of the carbene as $n_\pi \rightarrow p_\pi$ interactions are much less favourable due to the reduced flexibility of the seven-membered ring in compound **15**, and the presence of the strongly electron-withdrawing imidazolyl substituents at the imino group of **16**.
- The carbene-C–amino-N distance (d(C6–N3) = 1.323 (4) Å) which as in all structures of that type is shorter than the carbene-C–imino-N bond length (d(C6–N1) = 1.367(4) Å) reflecting the more efficient carbene-stabilization by the amino substituents.
- The C7–N2 distance of 1.352(4) Å which is much shorter than a C_{sp^2}–N_{sp^2} single bond (1.43 Å) [21] and even shorter than C6–N1 (see above) indicating some passing on of the electron demand of the carbene carbon along the C6–N1–C7–N2 atomic sequence. The carbene plane (N1, C6, N3, C31) is rotated by 60.7(2)° with respect to the meridian (Cr, C1, C3, C5), i.e., the carbene substituents and the *cis*-CO ligands are in an almost staggered arrangement.



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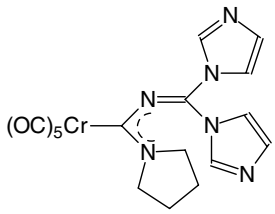


16

Table 2
^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR data[a]

Compound	^{1}H NMR	$^{13}C\{^{1}H\}$ NMR	Solvent
7[b]	7.60 (d, 2H, C_6H_4, ^{3}J(HH) = 7.2 Hz) 7.15 (d, 2H; C_6H_4, ^{3}J(HH) = 7.2 Hz) 6.80, 6.51 (2s, 1H, C=CH)	215.3, 214.9 (CO_{trans}), 213.6, 213.4 (CO_{cis}) 184.4, 179.8 (CN), 163.0 (C–F, ^{1}J(CF) = 248 Hz) 131.4, 131.3 (C=*C*H), 130.3, 126.2, 116.0 (C_6H_4), 110.7 (C=*C*Cl)	$CDCl_3$
8[c]	7.60 (d, 2H, C_6H_4, ^{3}J(HH) = 7.2 Hz) 7.49 (d, 2H, C_6H_4, ^{3}J(HH) = 7.3 Hz) 7.18, 6.75, 6.49 (3s, 2H, C=CH)	215.7, 215.1 (CO_{trans}), 213.5, 213.3 (CO_{cis}) 185.7, 180.7 (CN), 133.0, 132.6 (C=*C*H) 129.9, 128.5, 126.3, 126.0 (C_6H_4) 113.0, 111.9 (C=*C*Cl)	$CDCl_3$
9[c]	8.09 (d, 1H, Ar, ^{3}J(HH) = 7.8 Hz) 7.90 (d, 1H, Ar, ^{3}J(HH) = 7.8 Hz) 7.57 (d, 2H, Ar, ^{3}J(HH) = 7.2 Hz) 7.28 (m, 4H, Ar)	214.9 (CO_{trans}), 213.3 (CO_{cis}), 187.4 (CN) 135.0 (*C*=CCl), 140.4, 130.1, 127.8, 126.4, 124.4, 120.0 (Ar), 109.6 (C=*C*Cl)	$CDCl_3$
13[b]	7.12 (m, 2H, C_6H_4), 7.00 (m, 2H, C_6H_4) 3.78 (m, 2H, N–CH_2), 3.64 (d, 1H, C$H_2C_6H_4$, ^{2}J(HH) = 15 Hz), 3.47, 3.32 (2m, 6H, N–CH_2) 2.35 (dt, 1H, C$H_2C_6H_4$, ^{2}J(HH) = 15 Hz) 1.92, 1.66 (2m, 8H, C-CH_2CH_2-C)	232.6 (carbene C), 223.1 (CO_{trans}), 219.0 (CO_{cis}) 161.6 (d, C–F, ^{1}J(CF) = 231 Hz), 141.0 (N=C–N) 131.6–115.5 (C_6H_4), 54.5, 49.9, 47.5 (N–CH_2) 39.9 (*C*$H_2C_6H_4$), 25.5, 24.6 (C-*C*H_2*C*H_2-C)	$CDCl_3$
14[b]	7.12 (m, 2H, C_6H_4), 7.00 (m, 2H, C_6H_4) 3.76 (m, 4H, N–CH_2), 3.64 (d, 2H, C$H_2C_6H_4$, ^{2}J(HH) = 16 Hz), 3.45, 3.35 (2m, 12H, N–CH_2) 2.37 (dt, 2H, C$H_2C_6H_4$, ^{2}J(HH) = 16 Hz) 1.82, 1.65 (2m, 16H, C-CH_2CH_2-C)	232.4 (carbene C), 223.1 (CO_{trans}), 218.9 (CO_{cis}) 141.0 (N=C–N), 134.3–126.5 (C_6H_4) 54.4, 49.9, 47,6 (N–CH_2), 40.9 (*C*$H_2C_6H_4$) 25.4, 24.5 (C-*C*H_2*C*H_2-C)	$CDCl_3$
17[b]	7.50 (m, 8H, Ar), 3.37 [s, 3H, N-$(CH_3)_{exo}$] 2.35 [s, 3H, N-$(CH_3)_{endo}$]	Not measured	$CDCl_3$
19[b,d]	7.70, 7.49, 7.33, 7.16 (m, 8H, Ar) 3.91 [t, 2H, N-$(CH_2)_{exo}$], 2.62 [t, 2H, N-$(CH_2)_{endo}$], 1.71 [q, 2H, C-$(CH_2)_{exo}$-C] 1.60 [q, 2H, C-$(CH_2)_{endo}$-C]	286.9 (carbene C), 224.0 (CO_{trans}), 217.8 (CO_{cis}) 175.8 (ring C4), 141.2–120.8 (Ar), 95.0 (ring C5), 51.5 [N-$(CH_2)_{exo}$], 45.4 [N-$(CH_2)_{endo}$] 25.4 [C-(*C*$H_2)_{exo}$-C], 23.7 [C-(*C*$H_2)_{endo}$-C]	$CDCl_3$
20[c,d]	10.89 (s, 1H, NH) 7.95, 7.60, 7.45, 7.18 (m, 8H, Ar) 4.78 [t, 2H, N-$(CH_2)_{exo}$], 3.82 [t, 2H, N-$(CH_2)_{endo}$], 1.73 [q, 2H, C-$(CH_2)_{exo}$-C] 1.57 [q, 2H, C-$(CH_2)_{endo}$-C]	272.6 (carbene C), 223.5 (CO_{trans}), 217.8 (CO_{cis}) 174.8 (ring C4), 141.2–121.6 (Ar), 93.8 (ring C5), 51.9 [N-$(CH_2)_{exo}$], 46.0 [N-$(CH_2)_{endo}$] 24.8 [C-(*C*$H_2)_{exo}$-C], 23.1 [C-(*C*$H_2)_{endo}$-C]	DMSO-d_6
21[c,d]	8.02, 7.82, 7.69, 7.51 (m, 8H, Ar) 5.61 (s, 3H, Me) 4.65 [t, 2H, N-$(CH_2)_{exo}$], 4.13 [t, 2H, N-$(CH_2)_{endo}$], 3.19 [q, 2H, C-$(CH_2)_{exo}$-C] 2.90 [q, 2H, C-$(CH_2)_{endo}$-C]	268.1 (carbene C), 221.9 (CO_{trans}), 217.8 (CO_{cis}) 174.8 (ring C4), 141.3–121.4 (Ar), 90.6 (ring C5), 51.9 [N-$(CH_2)_{exo}$], 46.1 [N-$(CH_2)_{endo}$] 44.9 (Me), 24.8 [C-(*C*$H_2)_{exo}$-C], 23.1 [C-(*C*$H_2)_{endo}$-C]	DMSO-d_6
22[b,e]	8.00–7.00 (m, 45H, Ph) 4.79 (d + satellites, 2H, Ph_3PCH_2, ^{2}J(PH) = 10 Hz, $^{4}J(^{195}PtH)$ = 19 Hz)		MeCN-d_3
23[b,f]	7.8 (m, 15H, Ph), 7.50 (m, 30H, Ph) 8.03, 6.88 (2d, 2H, C_6H_4, ^{3}J(HH) = 9 Hz) 4.62 (dd, 1H, O–C*H*C_6H_4, ^{3}J(HH) = 12 Hz, ^{3}J(PH) = 3 Hz), 3.98 (dd, 1H, N–C*H*-PPh_3, ^{3}J(HH) = 12 Hz, ^{2}J(PH) = 17 Hz)		Acetone-d_6

[a] Chemical shifts, δ, as ppm downfield from solvent as internal standard.
[b] ^{1}H NMR: 250 MHz, $^{13}C\{^{1}H\}$ NMR: 62.8 MHz.
[c] ^{1}H NMR: 399.8 MHz, $^{13}C\{^{1}H\}$ NMR: 100.5 MHz.
[d] The pyrrolidine hydrogen atoms appear as triplets (t) and quasi-quintets (q) with very similar ^{3}J(HH) coupling constants of ca. 8 Hz (see, e.g., D.H. Williams, I. Fleming, Spektroskopische Methoden zur Strukturaufklärung, Georg Thieme Verlag, Stuttgart, 1979).
[e] $^{31}P\{^{1}H\}$ NMR (MeCN-d_3, 36.2 MHz): 17.2 + sat. ($CNCH_2PPh_3$, $^{4}J(^{195}PtP)$ = 25 Hz), 20.2 + sat. (*trans*-$Pt(PPh_3)_2$, $^{1}J(^{195}PtP)$ = 2166 Hz).
[f] $^{31}P\{^{1}H\}$ NMR (acetone-d_6, 36.2 MHz): 15.0 (ring-PPh_3), 22.8 + sat. at 61.8 and -16.0 (*trans*-$Pt(PPh_3)_2$, $^{1}J(^{195}PtP)$ = 2822 Hz).

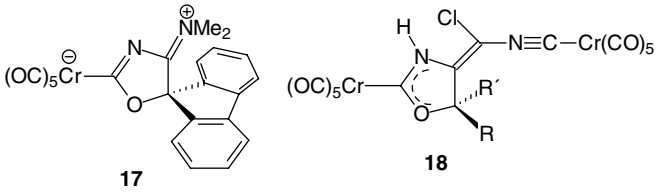
Table 3
Mass spectroscopic data of selected compounds [*m/z* (relative intensity)] (^{52}Cr, ^{35}Cl)

Compound	$[M]^+$	$[M-CO]^+$	$[M-2CO]^+$	$[M-3CO]^+$	$[M-4CO]^+$	$[M-5CO]^+$
7[a]	373(6)		317(7)	289(11)	261(19)	233(100)
8[a,b]	633(4)			549(1)	521(3)	493(11)
9[a]	429(11)		373(3)	345(7)	317(24)	289(100)
10[a]	347(14)	319(5)	291(12)	263(9)	235(21)	207(100)
11[a,c]	530(54)		474(3)	446(7)	418(20)	390(100)
13[d]	479(3)	451(16)		395(59)	367(16)	339(100)
14[d]	844(1)	816(2)	788(4)	760(16)	732(5)	704(12)
17[a]	454(28)		398(6)	370(7)	342(51)	314(100)
19[a]	480(11)		424(4)	396(5)	368(32)	340(100)
20[d]	481(93)[e]		424(24)[f]	396(16)[f]	368(96)[f]	340(71)[f]
21[d]	495(29)[e]		424(20)[g]	396(14)[g]	368(14)[g]	340(4)[g]

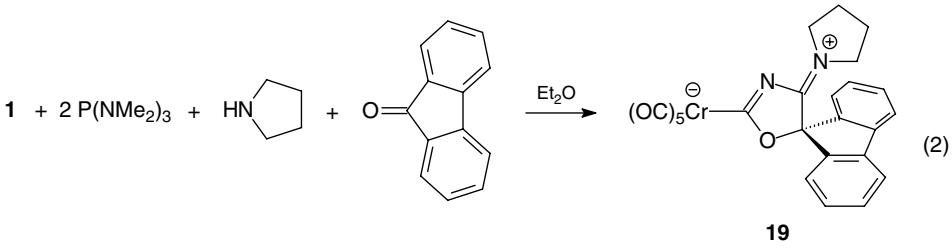
[a] EI (80 eV).
[b] Further peaks: 437(1) $[M-7CO]^+$, 409(1) $[M-8CO]^+$, 381(2) $[M-9CO]^+$, 353(3) $[M-10CO]^+$.
[c] Further peaks: 362(38) $[M-6CO]^+$, 334(10) $[M-7CO]^+$, 306(11) $[M-8CO]^+$, 278(41) $[M-9CO]^+$, 250(50) $[M-10CO]^+$.
[d] +FAB, Xe, DMSO, *m*-NO_2-benzyl alcohol.
[e] Complex cation.
[f] [Complex cation−*n*CO−H]$^+$.
[g] [Complex cation−*n*CO−Me]$^+$.

2.3. Reaction of *1* with tris(dimethylamino)phosphine and 9-fluorenone in the presence of pyrrolidine. X-ray structure of *19*

In 1987, a rather unusual heterocyclic carbene complex – **17** – had been isolated in our research group from the reaction of pentacarbonyl(trichloromethyl isocyanide)chromium (**1**) with $P(NMe_2)_3$ and 9-fluorenone [22]. Later attempts to repeat this experiment with miscellaneous carbonyl components O=CRR′ failed insofar, as instead of complexes of type **17**, a series of dinuclear carbene–isocyanide complexes (**18)** was obtained in the formation of which C^3–C^3 coupling must have occurred [23]. Mechanistic considerations in the context of the present study then made us add an amine component explicitly. With pyrrolidine as a fourth component and two equivalents of $P(NMe_2)_3$, **1** and 9-fluorenone in fact reacted to give the desired product **19** (Eq. (2)). (The emergence of **17**, accordingly, may be attributed to the presence of some free dimethylamine in tris(dimethylamino)phosphine (see above and 3.4); also transaminations by $P(NMe_2)_3$ definitely have no scarcity value [24].)



17 **18**



19

+ $[ClP(NMe_2)_3]Cl$ + $P(NMe_2)_3 \cdot HCl$

(2)

The new result can be explained by assuming an intermediate – isocyano(chloro)methylene-tris(dimethylamino) phosphorane – analogous to **3** (Scheme 1) which attacks the carbonyl carbon of 9-fluorenone. Of the two possibilities which exist for the negatively charged oxygen in **A** to carry on, (1) ring closure by addition to the isocyano group, or (2) formation of a P–O bond with elimination of phosphine oxide to give the same α-chloroalkenylisocyanide complex **9** as with PPh_3, now the first is verified. The

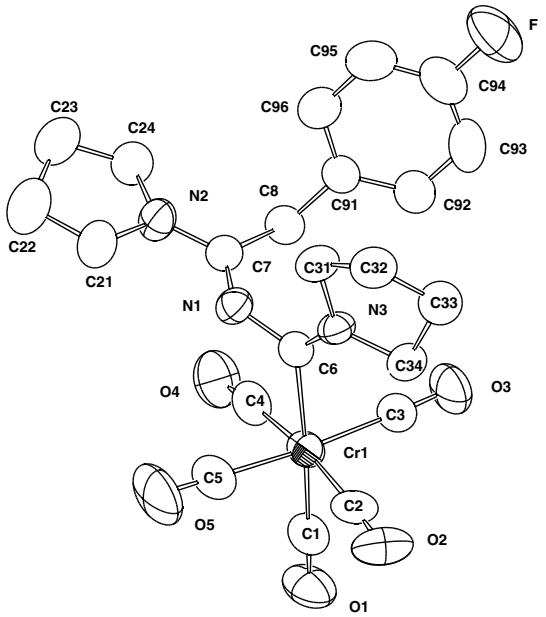
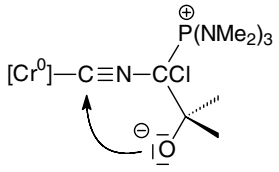


Fig. 1. Molecular structure of compound **13** with the crystallographic numbering scheme (ZORTEP-plot). The thermal ellipsoids have been drawn to include 50% probability. Selected bond lengths (Å) and angles (°): Cr1–C6 2.138(3), $(Cr1–CO_{cis})_{av}$ 1.889, Cr1–C1 1.863(4), C6–N1 1.367(4), C6–N3 1.323(4), N1–C7 1.279(4), C7–N2 1.352(4), C7–C8 1.517(4), C8–C91 1.518(4); $(C–Cr1–C)_{cis}$ 86.2(2)–96.17(13), $(C–Cr1–C)_{trans}$ 172.58(14)–176.0(2), Cr1–C6–N3 128.5(2), N1–C6–N3 112.6(3), C6–N1–C7 127.6(3), N1–C7–N2 118.9(3), N2–C7–C8 118.2(3), N1–C7–C8 123.0(3).

falling behind of the Wittig reaction appears comprehensible in view of a P atom rendered less oxygenophilic by its electron-rich amine-substituents.



A

In subsequent steps the labile phoshonio substituent in 4-position of the carbenoid oxazoline ligand is replaced by either a second molecule of the isocyano(chloro) ylid to give – after hydrolysis and HCl-elimination – the dinuclear C^3–C^3-coupled oxazolidin-2-ylidene/isocyanide species **18** [23], or by the secondary amine to give – again after HCl-elimination – **17** or **19**, respectively. A similar lability of a 4-triphenylphosphonio substituent leading to an unexpected C^3–C^3 coupling has already been observed in [3+2] cycloadditions between metallo-nitrile ylids of type **2** and triphenylketeneimine [25].

In this context, it is interesting to note, that in spite of their unusual betaïn-like bonding situation C-bonded 4-aminooxazolines such as **17** or **19** are stable compounds exhibiting in fact an extremely high tendency of formation. A host of complexes with exactly these types of ligands has thus been synthesized in recent years by very versatile and efficient three-component additions (3CC) between cyano complexes of various metals, isocyanides and carbonyl compounds [26]. Also notice, that there are close relations between the two sets of synthons: thus, complex **1** is the product of the radical alkylation of the cyano complex $[Cr(CN)(CO)_5]^-$ in chloroform, and the role of the isocyanide in the 3CC is clearly taken over by the trichloromethyl side chain of complex **1**, $P(NMe_2)_3$ and the amine in the present approach (Eq. (2)).

The wealth of information on related 3CC products we have at our disposal makes the discussion of the spectroscopic and structural data of the new compounds **17** and **19** a lot easier and shorter. While in the IR, the missing ν(NC) and new absorptions about 1640 cm^{-1} [ν(≻C═N≺)] and 1450 cm^{-1} [ν(N---C---O)] are at least of some diagnostic value, it is the exceptional low field ^{13}C NMR shift (**19**: δ 286.9) of the chromium bonded carbon atom which deserves underlining. More specific of the compounds in question is the appearance of two (**17**: δ 2.35, 3.37) and, respectively, four (**19**: δ 3.91, 2.62, 1.71, 1.60 [AA′BB′CC′DD′-system]) markedly different ^1H NMR signals for the exocyclic amino group, the latter of which

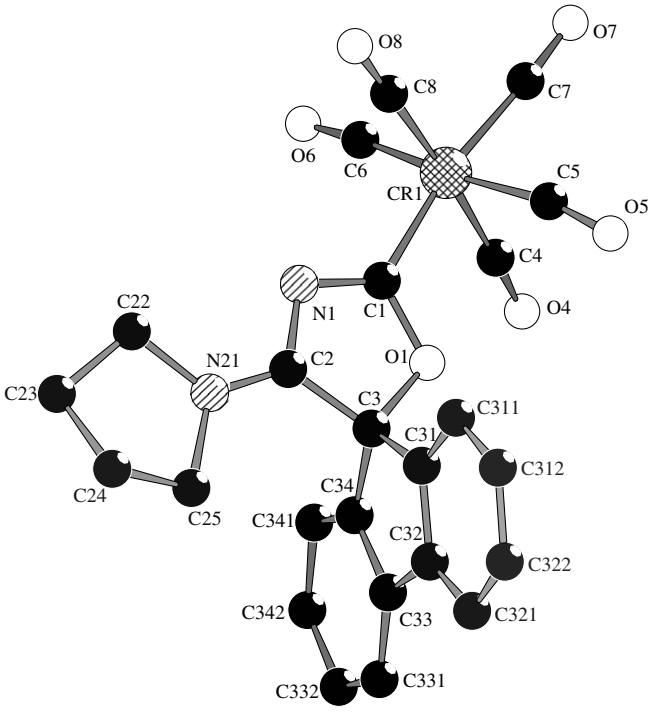


Fig. 2a. Molecular structure of compound **19** ('ball and stick'-model) with the crystallographic numbering scheme (DIAMOND-1.2 plot). Selected bond lengths (Å) and angles (°): Cr1–C1 2.033(3), $(Cr1–CO_{cis})_{av}$ 1.882, Cr1–C7 1.918(11), C1–N1 1.345(4), C1–O1 1.363(4), N1–C2 1.343(4), O1–C3 1.453(4), C2–C3 1.509(4), C2–N21 1.26(2); $(C–Cr1–C)_{cis}$ 85.4(6)–101.1(11), $(C–Cr1–C)_{trans}$ 170.2(10)–175.55(16), Cr1–C–O 169(3)–179.3(3), Cr1–C1–N1 129.6(2), Cr1–C1–O1 118.5(2), N1–C1–O1 111.1(17), C1–N1–C2 107.7(3), C1–O1–C3 109.7(2), N1–C2–C3 111.3(3), O1–C3–C2 99.5(2), C2–N21–C22 125.6(14), C2–N21–C25 122.2(14), C22–N21–C25 111.1(17).

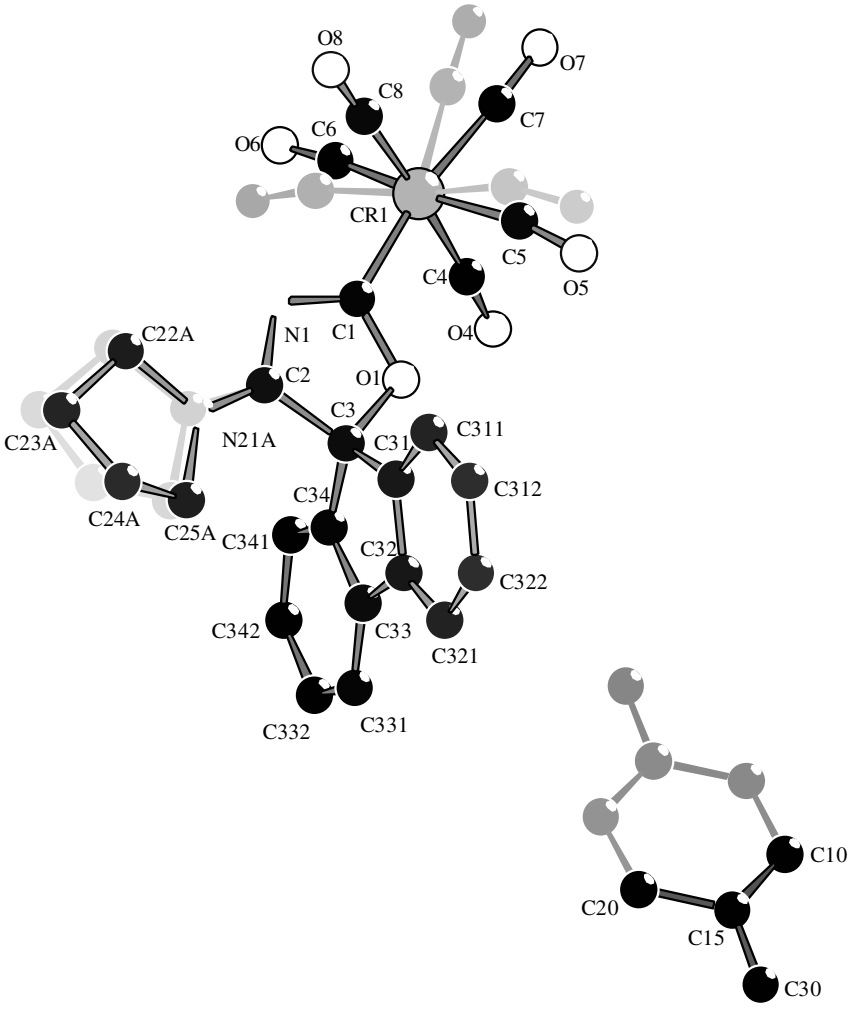


Fig. 2b. DIAMOND-1.2 plot of **19** and the solvent molecule with special emphasis of the disorder. The atoms in question are shaded.

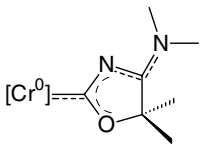
correspond with four lines in the ^{13}C NMR (Table 2). This clearly reflects an electronic situation which forces the iminium system into a rigid coplanar orientation with respect to the oxazoline ring thereby exposing one substituent, Me or CH_2-CH_2, respectively, to the magnetic influence of the perpendicularly arranged aromatic fluorenediyl [27].

The X-ray structure analysis is in full accord with this interpretation (Figs. 2a and 2b). The interplanar angle between the perfectly planar oxazoline ring – the maximal deviation of an atom (O1) from its best plane amounts to merely 6(2) pm – and the fluorene entity in fact measures 89.8(2)°. That the interaction pyrrolidine/fluorenediyl is also a repulsive one is born out by the two external angles about C2, N21–C2–N1 and N21–C2–C3, differing by as much as 10°. The most striking feature common to all species of this kind, however, is a sequence of similarly short bond distances extending across the oxazoline ring atoms O1, C1, N1 and C2 as well as the *exo*-N21. Coming up to only 1.26(2) Å the distance between the last-named is particularly short and probably indicative of an isolated C_{sp^2}–N_{sp^2} double bond though this value is to be taken with care due to some disorder in the pyrrolidine region (Fig. 2b and Section 3). In addition we are confronted with a Cr–C1 bond (2.033(3) Å) that is rather short for a carbanionic, respectively, carbene complex stabilized by two heteroatoms (cf., for instance, $Cr(CO)_5\{C(NMe_2)(OEt)\}$: *d*(Cr–$C_{carbene}$) = 2.133(4) Å [28]), obviously a further measure by which the entire system tries to compensate for the strong electron deficiency introduced into the heterocycle by the 4-ketiminium function.

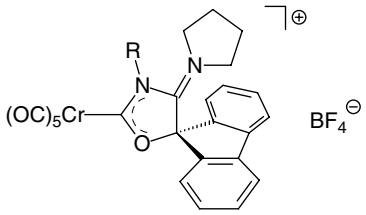
2.4. Protonation and alkylation of complex *19*

The spectroscopic and structural data collected on **19** (cf. Section 2.3) suggest its bonding to be described in terms of an extensive π-electron delocalization of the form **B** with still a considerable share of betaïn character. The question arose whether the heterocyclic ligand in spite of its partially positive charge would further react with electrophiles.

Treatment of **19** at 0 °C in dichloromethane with equimolar amounts of (a) HBF_4 and (b) $Me_3O^+BF_4^-$ gave brilliant yellow microcrystalline solids in an almost quantitative yield which after workup were identified as the cationic N,O-carbene complexes **20** and **21** (Section 3 and Tables 1–4).



B

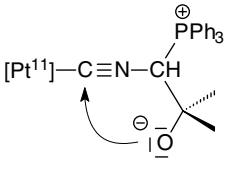


(**20**) R = H
(**21**) R = Me

The increased π-acceptor ability of the N-protonated and methylated ligands is evident from the ν(CO)-A_1-IR-absorptions of the new compounds which appear some 15 wavenumbers above that of **19**, and from the differences $\Delta\delta$ in the ^{13}C NMR shifts of the *cis*- and *trans*-CO ligands which decrease from 6.2 (**19**) to 5.7 (**20**) and 4.1 ppm (**21**), respectively [29]. As expected both, **20** and **21** show the same doubling of the signals of the aliphatic protons and of the carbon atoms of the pyrrolidine ring in the ^{1}H and ^{13}C NMR, respectively, as **19**, i.e., its free rotation about the C–N-axis is obviously hindered (see above).

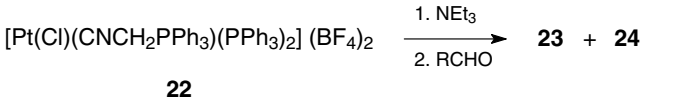
2.5. Oxazolin-2-ato complex formation in the system (isocyanomethylene)triphenylphosphorane-platinum(II) and p-nitrobenzaldehyde

In the preceding sections, it has been shown that the course of the reaction between **1**, triphenylphosphine and a carbonyl compound (aldehyde, ketone) is dramatically changed if PPh_3 is replaced by tris(dimethylamino)phosphine. While with the former α-chlorovinylisocyanide complexes **7**–**9** are obtained, $P(NMe_2)_3$ gives solely rise to oxazolin-2-ylidene(ato) species (**17**, **19**), for which we have put forward a reduced oxygenophilicity of the P-atom in **A**.



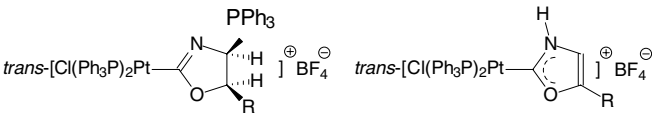
C

Here we report on the same competition for $-O^-$ in a slightly modified system **C**. Pentacarbonylchromium- and -tungsten-coordinated (isocyanomethylene)triphenylphosphorane had been reacted with various carbonyl compounds to give the corresponding complex vinylisocyanides, a result we erroneously also assumed for a similar reaction at platinum(II) in **22** [8]. Repeating the experiment we now found that the [3+2] cycloaddition gets the upper hand over the Wittig-type reaction in spite of the presence of triphenylphosphine (Eq. (3)). What tips the balance is the well-known activation towards nucleophilic attack isocyanides experience when bonded to higher valent metals, an effect thoroughly studied in their coordination and organometallic chemistry [30].



22

(3)



23 **24**

(**23**) R = 4-$C_6H_4NO_2$ (**24**) R = 4-$C_6H_4NO_2$

The resulting Pt complex **23** is sufficiently characterized by analysis, IR, ^{1}H and ^{31}P NMR spectra as well as conductivity measurements (Tables 1, 2 and 4, Section 3). According to the signal pattern of the oxazolin-2-ato hydrogens we are dealing with only one diastereoisomer, in fact the *cis*-arrangement of the two hydrogens, as gathered from the value of the ^3J(H,H′) coupling constant (12 Hz). The other isomer might well be present in the residue which makes up the bulk containing some *cis*-[$PtCl_2(PPh_3)_2$] along with [Pt(Cl)(CNMe)$(PPh_3)_2$]BF_4 and an impure fraction tentatively formulated as **24**. Loss of PPh_3 from the heterocycle – indicated here by a higher %N value and the lack of P-signals without ^{195}Pt satellites in the ^{31}P NMR – has been observed in several cases, one driving force being aromatization [25,31].

3. Experimental

All manipulations were performed under an atmosphere of pure argon using Schlenk-tube and vacuum techniques. The solvents were dried and distilled prior to use. Complex **1** was prepared according to a published procedure [32]. IR: Beckman IR 12 double beam infrared spectrometer and Perkin–Elmer 983 IR-spectrometer. NMR: Bruker AM 250, JEOL FX 90 and JEOL Lambda 400 spectrometers. MS: (EI) Varian Mat 711 (excitation energy 80 eV), (pos-FAB) Varian MAT CH 5 DF (neutral xenon source at 3 keV). Microanalyses (C, H, N) (Table 4): Heraeus CHN-Rapid elemental analyzer. Melting points (uncorrected): Gallenkamp MFB-595 apparatus. Conductivity measurements: Knick Digital Conductometer Model 600.

Table 4
Analytical and other data

Complex	Chemical formula molecular mass (g/mol)	Melting point (°C)	Yield (%)	Analyses (%)	C	H	N
7	$C_{14}H_5ClCrFNO_5$	93	72	Calculated	44.91	1.34	3.74
	373.60			Found	45.71	1.33	3.90
8	$C_{22}H_6Cl_2Cr_2N_2O_{10}$	107	63	Calculated	41.69	0.94	4.41
	633.15			Found	41.61	1.57	4.95
9	$C_{20}H_8ClCrNO_5$	115	71	Calculated	55.89	1.86	3.25
	429.67			Found	54.02	2.13	3.21
10	$C_8Cl_3CrNO_5$	85–86	4	Calculated	27.58	–	4.02
	348.4			Found	28.27	–	4.15
11	$C_{14}Cl_2Cr_2N_2O_{10}$	174 (dec.)	12	Calculated	31.66	–	5.28
	531.1			Found	31.39	–	5.21
13	$C_{22}H_{22}CrFN_3O_5$	88	66	Calculated	55.11	4.58	8.76
	479.43			Found	55.05	5.03	8.84
14	$C_{38}H_{40}Cr_2N_6O_{10}$	107	59	Calculated	54.04	4.73	9.95
	844.45			Found	52.95	5.39	9.32
17	$C_{22}H_{14}CrN_2O_6$	169 (dec.)	[a]	Calculated	58.16	3.11	6.17
	454.4			Found	57.75	3.20	6.12
19	$C_{24}H_{16}CrN_2O_6$	107	77	Calculated	59.96	3.33	5.83
	480.27			Found	59.67	3.66	5.82
20	$C_{24}H_{17}BCrF_4N_2O_6$	173 (dec.)	71	Calculated	50.07	2.99	4.92
	568.07			Found	50.30	3.51	5.07
21	$C_{25}H_{19}BCrF_4N_2O_6$	188	77	Calculated	51.54	3.26	4.81
	582.08			Found	49.38	3.69	5.02
22	$C_{56}H_{47}B_2ClF_8NP_3Pt + CH_2Cl_2$	187 (dec.)	81	Calculated	52.02	3.75	1.06
	1316.00			Found	51.86	3.91	1.14
23	$C_{63}H_{51}BClF_4N_2O_3P_3Pt + 1/2\ CH_2Cl_2$	158 (dec.)	18	Calculated	57.05	3.92	2.10
	1336.85			Found	57.27	4.01	2.20

[a] Not determined.

3.1. Preparation of $Cr(CO)_5CN–CCl{=}CRR'$ (7–9) (general procedure)

To a mixture of 336 mg (1.0 mmol) of **1** and 125 mg (1.0 mmol) of *p*-fluorobenzaldehyde [respectively 67 mg (0.5 mmol) of terephthaldehyde, respectively 180 mg (1.0 mmol) of 9-fluorenone] in 20 ml of diethylether is added dropwise at 0 °C a solution of 524 mg (2.0 mmol) of triphenylphosphine in 20 ml of diethylether. A precipitate of $[Ph_3PCl]Cl$ forms immediately, while the supernatant solution turns from yellow to orange. After warming to room temperature the solution is stirred for 24 h after which time the precipitate is filtered off and the solution is evaporated to dryness. The remaining residue is purified by chromatography on a silica-charged column (2×18 cm) with petrolether/ether (10/1) as eluent. In all cases, the second, intensely yellow to green fraction is collected. Evaporation of the solvent affords the products as mixtures of *E* and *Z* isomers. Recrystallization from diethylether/*n*-hexane (1/2) results in lemon-coloured needles (**7**) [respectively orange needles (**8**), or light green plates (**9**)].

3.2. Reduction of 1 with zinc. Complexes 10 and 11

Zinc powder (750 mg, 11.5 mmol) is suspended in a solution of 1.50 g (4.46 mmol) of **1** in 50 ml of diethylether, and the mixture is cooled to −40 °C. Argon-saturated glacial acetic acid (2 ml) is added, and the suspension is allowed to warm to room temperature. After stirring for 16 h the yellow precipitate is filtered off and extracted with ether (3×15 ml). The combined filtrate and extracts are evaporated to dryness, and the residue is extracted with *n*-pentane. Chromatography on silica gel (0.063–0.200 mm, Merck) results in three fractions the first of which is sublimed in high vacuum to give 30 mg of **10**; the second fraction contains traces of **11** contaminated with **10** and is disposed, while the third contains the main product $Cr(CO)_5CNMe$ (270 mg, 45%).

Action of zinc amalgam (in excess) on **1** (504 mg, 1.50 mmol) in 40 ml of ether leads to a red-orange solution the chromatographic work-up of which (see above) yields two yellow phases. Only the first is collected to give after recrystallization from dichloromethane/petrolether 50 mg (12%) of **11** as yellow plates.

3.3. Reactions of 7 and 8 with pyrrolidine. Preparation of complexes 13 and 14

To 372 mg (1.0 mmol) of **7** [respectively 316 mg (0.5 mmol) of **8**] in 15 ml of diethylether are added dropwise 0.25 ml (3.0 mmol) of pyrrolidine in 10 ml of diethylether. A white precipitate of pyrrolidine × HCl forms. After stirring for 4 h the precipitate is filtered off (G4-frit), and the solvent is removed in high vacuum. The residue is dissolved in a minimum amount of ether and chromatographed on neutral Al_2O_3 with *n*-hexane/ether (2/1) as eluent (2 × 18 cm column). The product is in the second fraction which is collected and taken to dryness. The pale yellow powder is recrystallized from *n*-hexane/ether (2/1) at −20 °C to give pale yellow prisms (**13**) [respectively yellow needles (**14**)].

3.4. Preparation of complexes 17 and 19

A solution of 672 mg of **1**(2.0 mmol) and 360 mg (2.0 mmol) of 9-fluorenone in 40 ml of diethylether is cooled to 0 °C. To this solution is added dropwise a mixture of 0.74 ml (4.0 mmol) of $P(NMe_2)_3$ and 2.0 mmol of the secondary amine [dimethylamine (90 mg) or pyrrolidine (0.17 ml), respectively] in 10 ml of diethylether. The colour of the solution changes to violet, and an oily material separates. The mixture is allowed to warm to room temperature and is stirred for further 2 h. The precipitate is filtered off and the filtrate is evaporated to dryness. The residue is purified by chromatography on a silica (respectively Al_2O_3-neutral: **19**) charged column (2 × 15 cm) with petrolether/ether (1/1) as eluent. The product containing second orange-yellow fraction is collected, and the solvent removed in vacuum. Recrystallization from toluene at −20 °C affords lemon needles (**17**) or intensely yellow crystals (**19**), respectively.

3.5. Preparation of complex 20

A solution of 480 mg (1.0 mmol) of **19** in 20 ml of dichloromethane is cooled to 0 °C and mixed with 0.2 ml (1.1 mmol) of an etheral solution of HBF_4 (54%). The cooling device is removed and stirring continued for 12 h at r.t. after which time the solvent is removed in high vacuum. The residue is stirred up in 20 ml of diethylether, collected on a frit (G4) and washed several times with 20 ml of ether each. The remaining brilliant yellow powdery solid is dried in vacuum and recrystallized at 0 °C from dichloromethane–diethylether (3/1) to give yellow needle-shaped crystals.

3.6. Preparation of complex 21

From 480 mg (1.0 mmol) of **19** and 170 mg (1.1 mmol) of trimethyloxonium tetrafluoroborate as described for **20**. Before evaporating the solvent, however, an excess of $[OMe_3][BF_4]$ is quenched with methanol (1 ml) to give yellow needle-shaped crystals.

3.7. Preparation of complex 23

3.7.1. trans-[Pt(Cl)(CNCH$_2$PPh$_3$)(PPh$_3$)$_2$](BF$_4$)$_2$ (22)

To a solution of 0.70 g (1.57 mmol) of $[CNCH_2PPh_3]PF_6$ [8] in 100 ml of dichloromethane are added 1.32 g (0.78 mmol) of $[Pt(\mu\text{-}Cl)(PPh_3)_2]_2(BF_4)_2$ [33]. After 12 h of stirring at r.t. the first milky suspension has almost become a clear solution which is filtered through Celite. The filtrate is concentrated in vacuo to about 40 ml, layered with 15 ml of ether and cooled to −15 °C. The compound separates as white crystals which are soluble in CH_2Cl_2 and acetonitrile. Molar conductivity: Λ_M (22 °C, 10^{-7} M, nitromethane) = 145 S mol^{-1} cm^2.

3.7.2. Reaction with p-nitrobenzaldehyde

The solution of 1.0 g (0.8 mmol) of **22** (see Section 3.7.1) and 0.12 g (0.8 mmol) of *p*-nitrobenzaldehyde in 50 ml of dichloromethane is mixed with ca. 0.14 ml (≈1 mmol) of triethylamine and stirred for 5 days in the dark. The solvent is removed and the solid residue transferred onto a column (2.5 × 15 cm) charged with silica/CH_2Cl_2. First the residue is washed with dichloromethane until the yellow colour of the washing liquids[2] has almost disappeared. Finally, elution of the product is carried out with a mixture of dichloromethane and acetone (1/3) resulting in a yellow phase which is taken to dryness and recrystallized from CH_2Cl_2–ether. Pale yellow microcrystals (0.19 mg) which are soluble in polar organic solvents.

3.8. X-ray structure determinations

Suitable single crystals of **13** were obtained from a solution of the complex in diethyl ether layered with *n*-hexane at −20 °C, those of **19** grew from a saturated toluene solution of **19** at 0 °C. The crystals were mounted on glass fibers and all geometric and intensity data were obtained with a STOE four circle diffractometer (compound **13**) and a STOE-IPDS 25 four circle diffractometer (compound **19**), respectively, using Mo Kα-radiation ($\lambda = 0.71073$ Å) and graphite-monochromators. An absorption correction (program DIFABS [34]) was applied to **19**, however, not to **13**. Both structures were solved by direct methods and developed using alternating cycles of full-matrix least-squares refinement and difference-Fourier synthesis (programs **13**: SHELXS-86, SHELXL-93 [35]; **19**: SHELXS-97, SHELXL-97 [36]). All non-hydrogen atoms were refined anisotropically, the hydrogens atoms isotropically in calculated positions, or in those suggested by the difference Fourier maps (fluorenediyl part of **19**), respectively. In **19** half a molecule of toluene per complex molecule was found which is

[2] A cursory workup of the CH_2Cl_2-solutions yielded fractions which were clearly identified as the hydrolysis product $[Pt(Cl)(CNMe)(PPh_3)_2]BF_4$ and *cis*-$[PtCl_2(PPh_3)_2]$. In addition there was ample evidence for an oxazolinatoplatinum species **24** which had lost its triphenylphosphonio substituent (see Section 2.5). Molar conductivity: Λ_M (22 °C, 10^{-7} M, nitromethane) = 109 S mol^{-1} cm^2.

Table 5
Selected crystal and data collection details for **13** and **19**

Compound	**13**	**19**
Chemical formula	$C_{22}H_{22}CrFN_3O_5$	$C_{24}H_{16}CrN_2O_6 + 1/2\ C_7H_8$
Formula mass (g mol^{-1})	479.43	526.47
Crystal size (mm)	$0.60 \times 0.32 \times 0.30$	$0.30 \times 0.30 \times 0.08$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	12.657(5)	12.925(2)
b (Å)	11.645(5)	11.615(1)
c (Å)	16.102(8)	17.405(2)
β (°)	106.18(4)	106.89(1)
Volume (Å^3)	2279.3(2)	2500.2(5)
Z	4	4
D_{calc} (g cm^{-3})	1.397	1.399
Absorption coefficient μ (cm^{-1})	5.47	5.03
Temperature (K)	293	100
Scan mode	ω–2θ	ω–2θ
2θ Range (°)	$2.19 \leqslant 2\theta \leqslant 27$	$2.14 \leqslant 2\theta \leqslant 25.15$
Reflections collected	4968	4411
Reflections with $[I \geqslant 2\sigma(I)]$	2428	2905
Number of variables	289	514
Final R indices	$R_1 = 0.0397$, $wR_2 = 0.0941$	$R_1 = 0.0464$, $wR_2 = 0.1103$
R indices (all data)	$R_1 = 0.1411$, $wR_2 = 0.1264$	$R_1 = 0.0798$, $wR_2 = 0.1201$
Goodness-of-fit on F^2	1.000	0.912
Residual electron density (e Å^{-3})	0.399/−0.274	0.537/−0.497

disordered in the crystal, however; statistical disorder between two positions each was also observed for some atoms within the CO ligand and the pyrrolidine ring region (Fig. 2b). Crystallographic data and selected data referring to the data collection and refinement are summarized in Table 5. The programs ZORTEP and DIAMOND-1.2 were used for Figs. 1, 2a and 2b, respectively.

4. Supplementary material

Additional data for the X-ray structure analyses have been deposited with the Cambridge Crystallographic Data Centre. CCDC 634690 and 634691 contain the supplementary crystallographic data for **13** and **19**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] W.P. Fehlhammer, F. Degel, H. Stolzenberg, Angew. Chem., Int. Ed. Engl. 20 (1981) 214–215.
[2] G. Beck, W.P. Fehlhammer, Angew. Chem., Int. Ed. Engl. 27 (1988) 1344–1347.
[3] W.P. Fehlhammer, G. Beck, J. Organomet. Chem. 369 (1989) 105–116.
[4] W.P. Fehlhammer, G. Beck, Chem. Ber. 122 (1989) 1907–1913.
[5] W.P. Fehlhammer, S. Ahn, G. Beck, J. Organomet. Chem. 411 (1991) 181–191.
[6] S. Ahn, G. Beck, W.P. Fehlhammer, J. Organomet. Chem. 418 (1991) 365–376.
[7] S. Ahn, W. Sperber, W.P. Fehlhammer, J. Organomet. Chem. 489 (1995) 27–34.
[8] G. Zinner, W.P. Fehlhammer, Angew. Chem., Int. Ed. Engl. 24 (1985) 979–980.
[9] W.P. Fehlhammer, G. Zinner, M. Bakola-Christianopoulou, J. Organomet. Chem. 331 (1987) 193–205;
G. Zinner, M. Bakola-Christianopoulou, W.P. Fehlhammer, in: R.B. King, J.J. Eisch (Eds.), Organometallic Syntheses, vol.4, Elsevier, Amsterdam, 1988, pp. 82–86.
[10] R. Appel, F. Knoll, W. Michel, W. Morbach, H.D. Wihler, H. Veltmann, Chem. Ber. 109 (1976) 58–70.
[11] R. Rabinowitz, R. Marcus, J. Am. Chem. Soc. 84 (1962) 1312–1313.
[12] M. Guy, J.T. Guy Jr., D.W. Bennett, Organometallics 5 (1986) 1696–1702.
[13] W.P. Fehlhammer, G. Beck, J. Organomet. Chem. 379 (1989) 97–106.
[14] D. Lentz, D. Preugschat, J. Chem. Soc., Chem. Commun. (1992) 1523–1524.
[15] R. Kunz, W.P. Fehlhammer, Angew. Chem., Int. Ed. Engl. 33 (1995) 330–332.
[16] W.P. Fehlhammer, G. Beck, Z. Naturforsch. B 44 (1989) 1414–1420.
[17] See also: K.H. Dötz, Chem. Ber. 113 (1980) 3597–3604.
[18] See also: M. Oki, Applications of Dynamic NMR-Spectroscopy to Organic Chemistry, VCH, Weinheim, 1985.
[19] H. Fischer, F.R. Kreissl, U. Schubert, P. Hoffmann, K.H. Dötz, K. Weiß, Transition Metal Carbene Complexes, VCH, Weinheim, 1985.
[20] H. Fischer, U. Schubert, R. Märkl, Chem. Ber. 114 (1981) 3412–3420.
[21] Interatomic Distances and Configuration in Molecules and Ions, Chemical Society, Special Publication, London, 1958.
[22] G. Beck, Dissertation, Freie Universität Berlin, 1987.
[23] Complex **18** (CRR′ = fluorenediyl) has been ascertained by X-ray structure analysis: S. Ahn, V. Langenhahn, W.P. Fehlhammer (in preparation).

[24] H.-D. Bock, in: M. Regitz (Ed.), fourth ed., Methoden der organischen Chemie (Houbel-Weyl), vol. E1, Thieme, Stuttgart, 1982, p. 313f.
[25] W.P. Fehlhammer, G. Zinner, G. Beck, J. Fuchs, J. Organomet. Chem. 379 (1989) 277–288.
[26] D. Rieger, S.D. Lotz, U. Kernbach, J. Fuchs, W.P. Fehlhammer, Chem. Ber. 126 (1993) 2243–2246;
D. Rieger, S.D. Lotz, U. Kernbach, C. Andre, J. Bertran-Nadal, W.P. Fehlhammer, J. Organomet. Chem. 491 (1995) 135–152.
[27] R.A. Pascal, C.G. Winans, D. van Engen, J. Am. Chem. Soc. 111 (1989) 3007–3010;
H. Günther, NMR-Spektroskopie, Georg Thieme Verlag, Stuttgart, Germany, 1973.
[28] G. Huttner, B. Krieg, Chem. Ber. 102 (1972) 67–81.
[29] B.E. Mann, B.F. Taylor, ^{13}C NMR Data for Organometallic Compounds, Academic Press, London, 1981.
[30] For e.g. L. Busetto, A. Palazzi, B. Crociani, U. Belluco, E.M. Badley, B.J.L. Kilby, L. Richards, J. Chem. Soc., Dalton Trans. (1972) 1800–1805;
E. Singleton, H.E. Oosthuizen, Adv. Organomet. Chem. 22 (1983) 209;
M. Tamm, F.E. Hahn, Coord. Chem. Rev. 182 (1999) 175–209;
R.A. Michelin, A.J.L. Pombeiro, M.F.C. Guedes da Silva, Coord. Chem. Rev. 218 (2001) 75–112.
[31] F.E. Hahn, M. Tamm, Organometallics 14 (1995) 2597–2600;
G. Zinner, G. Beck, V. Langenhahn, W.P. Fehlhammer (in preparation).
[32] W.P. Fehlhammer, F. Degel, Angew. Chem., Int. Ed. Engl. 18 (1979) 75–76;
W.P. Fehlhammer, F. Degel, G. Beck, Chem. Ber. 120 (1987) 461–469.
[33] W.P. Fehlhammer, W.A. Herrmann, K. Öfele, third ed., in: G. Brauer (Ed.), Handbuch der Präparativen Anorganischen Chemie, vol. III, Ferdinand Enke, Stuttgart, 1981, pp. 2015–2016.
[34] N. Walker, D. Stuart, Acta Crystallogr., Sect. A 39 (1983) 158–166.
[35] G.M. Sheldrick, SHELXS-86 and SHELXL-93: Programs for the Determination of Crystal Structures, Universität Göttingen, Göttingen, Germany, 1990, 1993.
[36] G.M. Sheldrick, SHELXS-97 and SHELXL-97: Programs for the Determination of Crystal Structures, Universität Göttingen, Göttingen, Germany, 1997.