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Reactions of "in-Situ" Generated $Cr(CO)_5CN–C(Cl)–PR_3$ (R = Ph, NMe_2) with Potential Dipolarophiles. New Examples of [3+2] Cycloadditions with Concomitant Interligand CC Bond Formation [1]

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Keywords: Cycloaddition; Heterocycles; Carbenes; Bridging ligands; Isocyanide ligands; Chromium and dichromium complexes

Abstract. The highly functional chromio nitrile ylides $Cr(CO)_5C{\equiv}N–C(Cl)–PR_3$ (R = Ph, NMe_2) (**2a, b**) form readily in mixtures of $Cr(CO)_5CNCCl_3$ (**1**) with the respective phosphanes. Their reactions without isolation with the acylating agent $Cr(CO)_5CN(C{=}O)Ar$ (Ar = C_6H_4-*p*-NO_2), $MeO_2CC{\equiv}CCO_2Me$, ketones ($R_2C{=}O$, R = Me, Et; 2R = 9-fluorenediyl) and phenyl isocyanate to give the Cl/COAr-substitution- (**6a**), alkyne insertion- (**10**) and [3+2] cycloaddition products (**13**, **14**) are described. Formation of the latter is accompanied by an interligand CC coupling with loss of $P(NMe_2)_3$ and $OP(NMe_2)_3$ (after hydrolysis). Their reactions are compared with those of the parent compounds L_nMCN–C(**H**)–PPh_3.

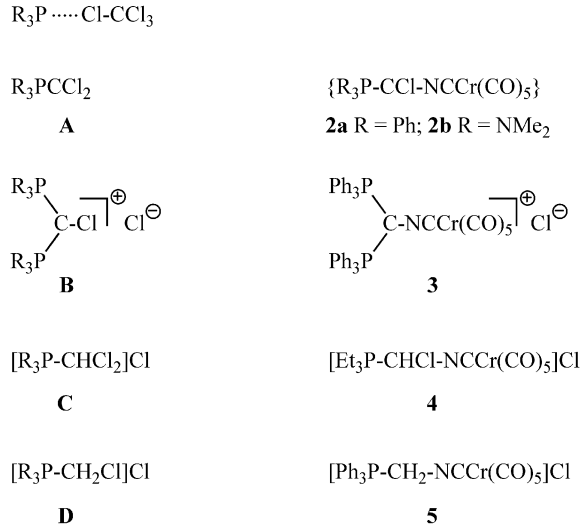
Introduction

Trichloromethyl isocyanide is one of the exciting small molecules with an inexhaustible reactivity potential on top. To date it only exists as a ligand in $Cr(CO)_5CNCCl_3$ (**1**) whose synthesis from $[Cr(CN)(CO)_5]^-$ and aryldiazonium ions in $CHCl_3$ by what we call "radical alkylation of cyanido complexes" obviously makes special demands on the redox properties not met by other organometallics [2, 3]. Reactions of **1** with nucleophiles (amines, thiols) generally set in at the isocyanide carbon atom (C^1) followed by successive Cl-substitution at C^3 [4, 5]. Occasionally only the C^1 atom remains of the original isocyanide forming new isocyanide or diaminocarbene complexes with the amine reactant [6, 7]. Imidazole, in contrast, interacts with C^3 exclusively giving rise to pentacarbonyl[tris(imidazolyl)methyl isocyanide]chromium [8].

$Cr(CO)_5C^1{\equiv}N{-}C^3Cl_3$

1

From reactions with phosphanes, correspondingly, P-functionalized methylisocyanide complexes result, though the site of primary attack is certainly not C^3 but the chloro substituents [9]. This as well as the nature of the species that subsequently form can easily be deduced from what is known to occur in *Appel*'s two-component-system CCl_4/PR_3 [10]. A comparison of the organoelement with the organometallic series is shown in Scheme 1.



Scheme 1. Species generated in mixtures of CCl_4/PR_3 (left column) or **1**/phosphanes, respectively (right column) (see text).

Depending on the stoichiometry and the reaction conditions – such as the presence of traces of water – compounds **A**–**D** were identified, all of which have organometallic counterparts **2**–**5**. Only compound **2** has not been isolated as such, but the trapping of **2a** in Wittig-type reactions with carbonyl

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compounds to give the corresponding α-chloroalkenyl isocyanide complexes proves its intermediary existence [1]. As metallo-nitrile ylides, capable of undergoing [3+2] cycloadditions, compounds **2** and **5** (after deprotonation) were of particular interest, the more as our synthetic access to **5** [and $Cr(CO)_5CNCHPPh_3$] so far required several tricky steps through free functional isocyanides lacking metal stabilization [11, 12]. "In situ"-generated **2b** has already been reported to react with ketones in the presence of secondary amines affording that sort of [3+2] cycloaddition products (vide infra and lit. [1]).

This paper presents further reactions of the chloro-substituted chromio-nitrile ylides **2,** which were carried out in order to confirm their intermediary existence, to investigate the role of the chlorine atom and to demonstrate the dependence of the reaction course on the nature of the phosphane.

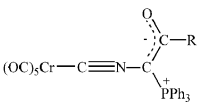
Results and Discussion

1. Reaction with $Cr(CO)_5CNC(=O)C_6H_4$-p-NO_2

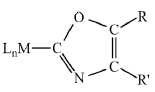
Acylisocyanide complexes such as $Cr(CO)_5CNC(=O)C_6H_4$-*p*-NO_2 are known to act as mild acylating agents towards various kinds of nucleophiles. Its reaction with **2a**, prepared "in situ" from **1** + 2 PPh_3, proceeds with elimination of the chlorine atom (formally as Cl^+) at C^3 to give complex **6a**. Obviously, this reduction (dechlorination) is the preferred way of stabilization for the presumed primary addition product. A third equivalent of PPh_3 is needed, which eventually reappears in the salt-like (Ph_3PCl^+) yet partially hydrolyzed precipitate together with the leaving group $[Cr(CN)(CO)_5]^-$.

The nature of **6a** is unequivocally settled by its spectroscopic data (Experimental Section), which perfectly agree with those of **6b**, the product of the reaction of $Cr(CO)_5CN–CH–PPh_3$ with trifluoroacetic acid anhydride [13]. Note that the formation of **6b** required the abstraction of H^+ by a base, which usually was the ylide itself ("Umylidierung"). The CN stretching vibrations [**6a/b**: 2129 m/2127 m cm^{-1}] as well as the ^{13}C NMR spectroscopic shifts of the isocyano (**6a/b**: δ = 166.2/168.7), the ylidic (**6a/b**: δ = 77.2/70.8) and the acyl carbon atoms (**6a/b**: δ = 183.2/172.1) are almost identical with the latter two existing as doublets (or even as *pseudo*-dd's) because of coupling with ^{31}P (and ^{19}F). A surprising difference, however, turns up in the $\nu(C=O)_{acyl}$ values [**6a/b**: 1695 m/1596 s, 1584 s, 1571 m (?) cm^{-1}]; still there is no doubt that the strong absorption at 1526 cm^{-1} must be assigned to the antisymmetric stretching of the NO_2 substituent [14].

In neither case the conceivable cyclization to a 4-phosphonio-oxazolatochromium species (**7**) took place, which is certainly a consequence of the interplay of the stabilization effect of chromium(0) on the isocyano group and the highly electron-deficient substitution on C^3 and C_{acyl}, which reduces the nucleophilicity of the acyl oxygen atom. That acylium ions are able to act as dipolarophiles towards metallo-nitrile ylides was shown earlier by the synthesis of **8** from $[Pt(Cl)(CNCH_2CO_2Et)(PPh_3)_2]BF_4$, NEt_3 and PhCOCl [15].



6a R=C_6H_4-*p*-NO_2; **6b** R=$COCF_3$



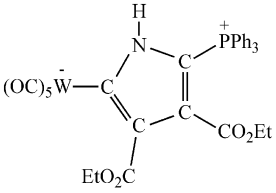
7 L_nM=$(OC)_5Cr$, R=C_6H_4-*p*-NO_2, R'=PPh_3

8 L_nM=$(Ph_3P)_2(Cl)Pt$, R=Ph, R'=CO_2Et

2. Reaction with $MeO_2CC{\equiv}CCO_2Me$

Again we compare the reaction with acetylene dicarbonicacid diester of the "in situ" generated chloro derivative **2a** with that of the parent compound $M(CO)_5CN–CH–PPh_3$ (where M = W): whereas the latter gave rise to the betain-like 4-phosphoniopyrrol-2-ato complex species **9** [13], in the case of **2a** all evidence points to the fact that 1,3-migration of the PPh_3 group or, respectively, insertion of the acetylene into the P–C bond had occurred. The main driving force for the cyclization to **9** probably is the ring aromatization, which requires the C^3–H bond to be cleaved, a process not feasible for **2a**. Here, the primary addition product with $MeO_2C–C{\equiv}C–CO_2Me$ stabilizes by rearrangement into the well-known α-chloroalkenyl isocyanide structural unit [1] (cf. Section 3) and a new phosphorus ylide, which is much less reactive because of extensive conjugation. This also explains why the final product **10** does not show tendency towards ring closure at all.

An unequivocal proof for both structural units mainly arises from the characteristic ^{13}C NMR spectroscopic data of the isocyano, the chlorine carrying and the ylidic carbon atoms; due to its bonding to phosphorus the latter appears as a doublet with the expected order of magnitude for $^1J(P,C)$ (Experimental Section).



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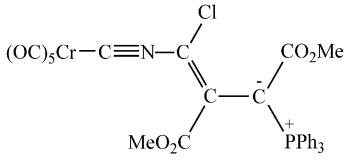


10

Very indicative of the P-ylidic nature of **10** also is a $\delta(^{31}P)$ of 20.3, particularly in comparison with a shift of δ = 9.5 for the phosphorus resonance in **9**. The rather low IR spectroscopic frequency of the CN stretching vibration is typical for isocyano groups linked to a sp^2 carbon atom. The assignment of $\nu(C=C)$, on the other hand, is questionable; however, there is indirect evidence in the form of a doubling of the ^{13}C signals for $(CO)_{trans}$ and $(CO)_{cis}$ which results from the presence of *E* and *Z* isomers. Similar observations including doubled CN resonances have been made on α-chloroalkenyl isocyanide complexes $Cr(CO)_5CNC(Cl)=CRR'$ [1].

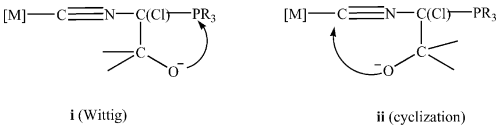
To the best of our knowledge, this is the first example of an alkyne insertion into a $C–P_{ylide}$ bond.

3. [3+2] Cycloaddition and C^3=C^3 Bond Formation in the Three-Component System [1/P(NMe$_2$)$_3$/Dipolarophile]: Dichromium Complexes with Carbene-Isocyanide Bridging Ligands

3.1 Ketones as Dipolarophiles

The mentioned α-chloroalkenyl isocyanide complexes were synthesized from **2a** and ketones [1]. Modification of the phosphane component led to an extension of this chemistry with widely differing results, which are summarized below.

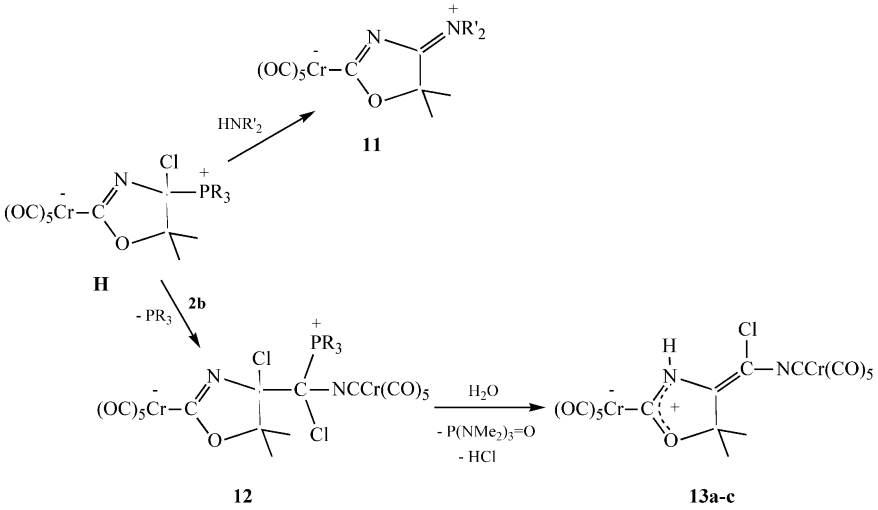
In the first step, the "in situ" generated compound $Cr(CO)_5CN–CCl–PR_3$ (R = Ph, NMe_2) attacks the carbonyl carbon atom. Which of the two possible consecutive processes then occurs – **i** to give α-chloroalkenyl isocyanide (and phosphane oxide) or **ii** leading to oxazolin-2-ylidene(ato) complexes – depends on the relative oxygenophilicity of the phosphorus atom. As this is less pronounced in the R = NMe_2 case, the [3+2] cycloaddition is preferred, ending up with the heterocyclic products **11** (with a secondary amine as fourth component) [1] and **12** or **13**, respectively (in the absence of amine) [Equation (1)].



(In parentheses it should perhaps be pointed out that in principle there is a second factor strongly determining the reaction course **i** or **ii**, viz. the electrophilicity of the isocyano group, which can be adjusted by proper choice of the metal; in the platinum(II) complex $[Pt(Cl)(CN\text{-}CH\text{-}PPh_3)(PPh_3)_2]^+$ the parent 1,3-dipole is sufficiently activated to undergo [3+2] cycloadditions with aldehydes in spite of the presence of PPh_3 [1]).

It stands to reason that **11** and **12** are formed via the same intermediate **H**. In the decisive step, the phosphonio substituent in the 4-position of the latter is replaced either by the secondary amine to give – after HCl-elimination – **11**, or by a second molecule of the isocyano(chloro) ylide to give – presumably via **12** – the "mixed" C=C-linked μ-oxazolin-2-ylidene/α-chloroalkenyl isocyanide bis(pentacarbonylchromium) complexes **13** [Equation (1)].

For both types of products striking parallels can be drawn to earlier findings in our laboratories. Thus, a reaction of the parent metallo-nitrile ylides $M(CO)_5CNCHPPh_3$ (*M* = Cr, W) with triphenylketeneimine resulted in an exceptional lability towards substitution of the 4-PPh_3 group of the heterocyclic primary product **I**, which led to the C–C coupled dinuclear intermediate **J** and further to **K** [Equation (2)] [16]. As for **11**, a host of such 4-amino-Δ^3-oxazolin-2-ylidene complexes that exhibit an extremely high tendency of formation had already been synthesized by very versatile and efficient three-compo-



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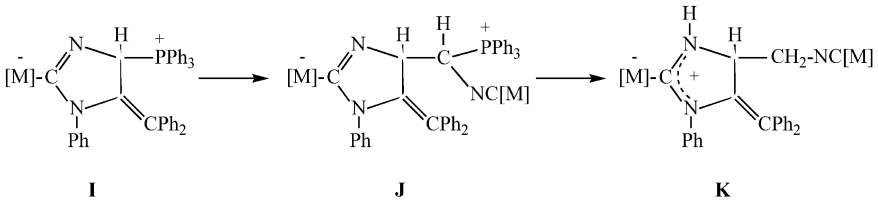

(2)

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nent additions (3CC) between cyanido complexes, isocyanides and carbonyl compounds [17].

In order to avoid hydrolysis of the presumed intermediate **12**, a work-up procedure without chromatography was chosen for the reaction with fluorenone. As is distinct from the needle-shaped crystals of complex **13a**, we now obtained cubic ones whose IR spectrum clearly lacked a ν(NH) band. Though the compound was analyzed correctly as **12** (R_2 = fluorenediyl), the X-ray structure determination only showed complex **13a** (see below). Obviously slow hydrolysis also occurs in the solid during crystal manipulation.

Complexes **13** form *E* and *Z* isomers, which exist in a ratio of ≈ 1:1 according to the IR spectra. Because of their similar R_f values, their separation aroused severe problems requiring repeated chromatography and fractional recrystallization. For this reason we refrained from a separation of the isomers of **13c**.

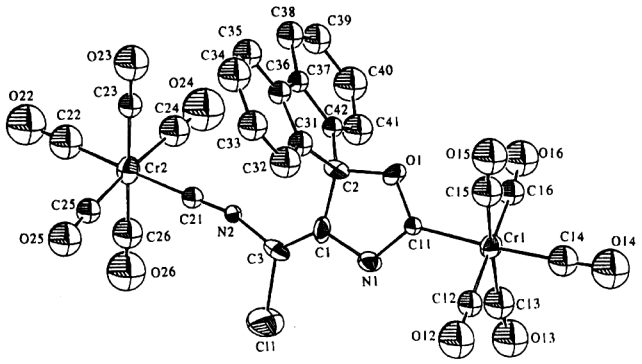


Figure 1. Molecular structure of compound **13a** with the crystallographic numbering scheme (ORTEP plot). The thermal ellipsoids have been drawn to include 50 % probability. Selected bond lengths /Å and angles /°: Cr1–C11 1.98(3), Cr1–C14 1.78(3), $(Cr1–C_{cis})_{av}$ 1.86, Cr2–C21 1.90(3), Cr2–C22 1.79(3), $(Cr2–C_{cis})_{av}$ 1.86, C11–O1 1.30(3), C11–N1 1.39(3), N1–C1 1.41(3), C1–C2 1.50(4), C2–O1 1.45(4), C21–N2 1.16(4), N2–C3 1.39(3), C3–Cl 1.69(3), C3–C1 1.32(5), N1···O2 2.64(3); Cr1–C11–O1 124(2), Cr1–C11–N1 130(2), N1–C11–O1 107(2), C11–N1–C1 113(2), N1–C1–C2 103(2), C1–C2–O1 103(2), C2–O1–C11 114(2), Cr2–C21–N2 178(3), C21–N2–C3 160(3).

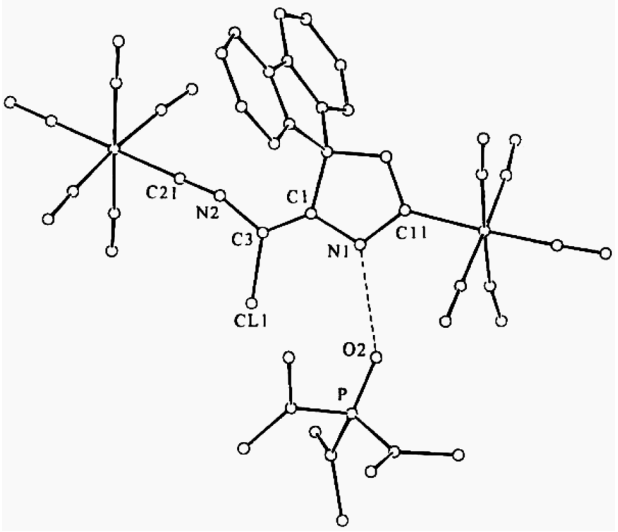


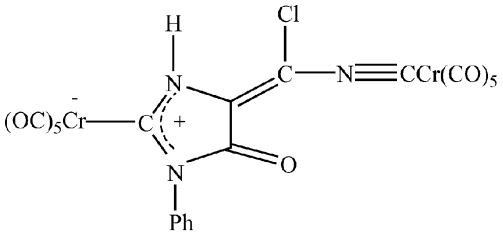
Figure 2. Asymmetric unit of **13a** + $O=P(NMe_2)_3$ with N1–H···O2 hydrogen bridge.

The IR spectra of the *E* and *Z* isomers of **13a** and **13b** exhibit slightly different ν(NH), ν(CN) and ν(C=C) absorption bands; it is not possible, however, to tell to which configuration the individual bands belong. All ν(CN) bands are of low intensity and fall in the narrow range of 2115–2125 cm^{-1}, which is characteristic for α-chloroalkenyl isocyanide complexes of Cr^0 [1]. The poor solubility of the new compounds prevented us from carrying out more extensive NMR spectroscopic measurements (Experimental Section).

As mentioned above, X-ray structure analysis of a supposed intermediate **12** came up with the structure of **13a** instead, which coexists with the byproduct $P(NMe_2)_3=O$ of its hydrolysis in the crystal. Figure 1 shows an ORTEP drawing of the molecular structure of **13a** with pertinent bonding parameters, whereas Figure 2 depicts an asymmetric unit containing the hydrogen-bonded pair of **13a** + $O=P(NMe_2)_3$. The distance between O2 of the phosphane oxide and N1 of the heterocycle amounts only 2.64(3) Å, this means we deal with a rather strong NH···O bond according to the range of bond lengths (2.50–2.7 Å) allocated to this category in the literature [18]. Relative to an average N,O-carbene complex the Cr1–C11 distance of 1.98(3) Å is unusually short as is the C11–O1 bond length [1.30(3) Å], which is even shorter than the $C_{carbene}$–N bond length [C11–N1: 1.39(3) Å] [19]. An N1–C1 bond of similar length, an exocyclic isolated CC double bond and two single bonds (C1–C2, C2–O1) to and from the ketone carbon atom (C2) complete the stereochemical picture, which can be understood as a consequence of the presence of the electron-withdrawing chloro(isocyano)vinylidene substituent in the 4-position of the heterocycle though the poor quality of the structure prevents a more detailed interpretation. For comparison, however, the formally carbanionic nature of the N-analogue **11** (and related 3CC products) and the extensive conjugative interaction along the O–$C_{carbene}$–N–C–N(*exo*-ammonium) atomic sequence, which results in practically identical bond lengths, should be noted [1, 17]. The isocyanide complex part is inconspicuous with the exception of the C21–N2–C3 angle of 160(3)° deviating considerably from linearity. Non-linear [*M*]C≡N–C arrangements of terminally coordinated isocyanides were found in complexes both with particularly electron-deficient ligands such as $(OC)_5Cr–CN–C(=NCF_3)–NC–Cr(CO)_5$ [C–N–C 167.8(5), 167.2(7)°] and with particularly electron-rich metal components, e.g., *trans*-$[Mo(CNMe)_2(dppe)_2]$ [C–N–C 156(1)°] [20]. Interesting deviations from the expected linearity of the structural element [*M*]–C≡N–[*M*'] also occur in supercomplexes of the type $(NEt_4)_2[Si\{N{\equiv}C–Cr(CO)_5\}_6]$ [C–N–C 172.8(3), 168.5(3)°] or $(NEt_4)_3[Ni\{N{\equiv}C–W(CO)_5\}_5]$ [C–N–C 164(3), 156(3), 150(4)°] [21]. In this case the bending might be a consequence of the steric repulsion between the fluorene group and *cis*-CO ligands on Cr2. At the Cr1 site it is the largely staggered orientation of the carbenoid heterocycle with respect to the *cis*-CO ligands (interplanar angle: 39°), which ensures steric relief.

3.2 Reaction with PhN=C=O

The reaction of phenyl isocyanate with the "in situ"-generated chromium coordinated isocyano(chloro)methylenephosphorane $(OC)_5Cr–CN–CCl–P(NMe_2)_3$ follows exactly the stoichiometry and mechanism of the reaction with ketones (cf. 3.1), i.e., the final product must be formulated as **14**. No attempts have been made to isolate the dinuclear analogue of **12** prior to hydrolysis.



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As in the case of **10**, the ^{13}C NMR spectroscopic data were extremely useful for the detection of special structural elements such as the α-chloroalkenyl isocyanide part with its characteristic narrow δ ranges for the isocyano (180–187) and C–Cl carbon atoms (113 ± 3). Two sets of CO signals – the one at higher field (δ = 215.1, 214.1) presumably arising from the isocyanide-coordinating $Cr(CO)_5$ group – in combination with two ν(CO)-A_1 IR features prove the dinuclear nature of **14**, yet unlike in **10** there is no further doubling of lines, which could be associated with *cis*/*trans* isomerism. As for the carbene complex part, neither the $C_{carbene}$ signal nor a ν(NH) band has been found; the NH group might be involved in strong hydrogen bonding as established in the crystal structure of **13a**, a possible counterpart could be the exocyclic amido oxygen atom of a neighboring molecule.

In comparison, no C^3C^3 coupling through phosphane substitution with a second molecule of the ylide occurs in [3+2] cycloadditions between the parent metallo-nitrile ylids L_nM-CNC*H*PPh_3 (ML_n = $Pt(Cl)(PPh_3)_2$, $Cr(CO)_5$, $W(CO)_5$, BPh_3) and isocyanates; as in the case of L_nM-CNC*H*R (R = Tos, CO_2Et) the primary product gains stability by a formal C4 to N3 -shift of the proton affording aromatic imidazol-5-olat-2-ylidene species [11, 22–25]. Even with these apparently more simple reagents, however, one has to grapple with diverse complications such as the formation of site-isomeric oxazole derivatives or 1:2 (ylide/isocyanate) addition products [22, 26].

Experimental Section

All manipulations were performed under pure argon using Schlenk-tubes and vacuum techniques. The solvents were dried and distilled prior to use. Complex **1** was prepared according to a published procedure [2]. Silica gel (100–200 μm) from ICN and Al_2O_3 90 active (neutral, 0.063–0.200 mm) from Merck were used for column chromatography. 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): Heraeus CHN-Rapid elemental analyzer. Melting points (uncorrected): Gallenkamp MFB-595 apparatus.

Pentacarbonyl[isocyano(*p*-nitrobenzoyl)methylenetriphenylphosphorane]chromium (6a): A solution of triphenylphosphane (524 mg, 2.0 mmol) in diethyl ether (10 mL) was added dropwise at room temp. to a mixture of **1** (336 mg, 1.0 mmol) and pentacarbonyl(*p*-nitrobenzoylisocyanide)chromium (368 mg, 1.0 mmol) in diethyl ether (20 mL). The orange-red solution lightened, and a precipitate ($[PPh_3Cl]Cl$) formed. After stirring for another 4 h, the precipitate was filtered off (G4 frit) and the solvent was removed in high vacuum. The oily residue was dissolved in a small amount of diethyl ether and purified by column chromatography on neutral Al_2O_3 using diethyl ether/petroleum ether (1:1) as eluent. The orange-red second fraction was collected and the solvents were evaporated to dryness under high vacuum. Recrystallization of the orange-red powder from toluene at –20 °C gave orange needles in 63 % yield. M. p. 117 °C. $C_{32}H_{19}CrN_2O_8P$ (642.33): calcd. C 59.83, H 2.95, N 4.36; found C 59.31, H 3.56, N 4.57. **IR** (KBr): $\tilde{\nu}$ = 3064 m [$\nu(CH)_{aryl}$], 2129 m [ν(CN)], 2059 s, 1927 vs, br. [ν(CO)], 1695 m [$\nu(CO)_{acyl}$], 1526 s [$\nu_{as}(NO_2)$], 1346 s [$\nu_s(NO_2)$] cm^{-1}. **^{1}H NMR** ($CDCl_3$, 250 MHz): δ = 8.26 (m, 2 H, C_6H_4), 7.99 (m, 2 H, C_6H_4), 7.65 (m, 15 H, Ph). **^{13}C{^{1}H} NMR** ($CDCl_3$, 250 MHz): δ = 217.6 (CO_{trans}), 214.7 (CO_{cis}), 183.2 (d, CO_{acyl}), ^2J(P,C) = 18 Hz, 166.2 (CNR), 148.5–121.4 (C_{aryl}), 77.2 (d, CN*C*P), ^1J(P,C) = 135 Hz. **^{31}P{^{1}H} NMR** ($CDCl_3$, 400 MHz): δ = 20.6. **MS** (+FAB, Xe, DMSO, 3-nitrobenzylalcohol), *m*/*z* (int. %): 643 (13) $[M]^+$, 559 (18) $[M – 3CO]^+$, 530 (21) $[M – 4CO]^+$, 502 (18) $[M – 5CO]^+$.

Synthesis of 10: A solution of triphenylphosphane (524 mg, 2.0 mmol) in diethyl ether (10 mL) was added dropwise at room temp. to a mixture of **1** (336 mg, 1.0 mmol) and acetylenedimethylcarboxylate (124 mg, 1.0 mmol) in diethyl ether (20 mL). The yellow solution turned dark red, and a precipitate ($[PPh_3Cl]Cl$) formed immediately. After stirring for another 4 h, the precipitate was filtered off (G4 frit) and the solvent was removed in high vacuum. The dark red resinous residue was dissolved in the least possible amount of diethyl ether and purified by column chromatography on neutral Al_2O_3 using diethyl ether/petroleum ether (1:2) as eluent. The orange second fraction was collected and the solvents were evaporated to dryness under high vacuum resulting in an orange-yellow microcrystalline solid, which already was analytically pure. M.p. 113 °C, yield: 73 %. $C_{31}H_{21}ClCrNO_9P$ (669.76): calcd. C 55.59, H 3.13, N 2.09; found C 56.21, H 3.66, N 2.18. **IR** (KBr): $\tilde{\nu}$ = 3059 w [$\nu(CH)_{aryl}$], 2950 m [$\nu(CH)_{alkyl}$], 2119 m [ν(CN)], 2041 s, 1998 s, 1944 vs, br. [ν(CO)], 1719 s [$\nu(CO_2Me)$], 1626 m [ν(C=C)] cm^{-1}. **^{1}H NMR** ($CDCl_3$, 250 MHz): δ = 7.72 (m, 15 H, Ph), 3.60 (s, 3 H, Me), 3.45 (s, 3 H, Me). **^{13}C{^{1}H} NMR** ($CDCl_3$, 250 MHz): δ = 215.7, 215.3 (CO_{trans}), 213.5, 213.2 (CO_{cis}), 186.9 (=C*C*O2Me), 180.6 (CrCN), 168.1 (d, PCCO_2Me), ^2J(P,C) = 12 Hz, 133.7–127.3 (C_{aryl}), 113.1 (C=CCl), 52.2, 50.1 (OCH_3), 46.1 (d, P*C*CO_2Me), ^1J(P,C) = 128 Hz. **^{31}P{^{1}H} NMR** ($CDCl_3$, 400 MHz): δ = 20.3. **MS** (+FAB, Xe, DMSO, 3-nitrobenzylalcohol), *m*/*z* (int. %): 670 (3) $[M]^+$, 586 (3) $[M – 3CO]^+$, 558 (7) $[M – 4CO]^+$, 530 (41) $[M – 5CO]^+$, 451 (37) $[M – 5CO – Cr]^+$.

General Procedure for the Complexes 13a-c: A stoichiometric amount of the respective ketone was added to a solution of **1** (1.0 g, 2.98 mmol) in CH_2Cl_2 (40 mL) and the mixture was cooled to –60 °C. To this suspension a solution of $P(NMe_2)_3$ (1.08 mL, 5.94 mmol) in CH_2Cl_2 (10 mL) was added dropwise whereupon the mixture quickly turned dark violet. The cooling device was removed and stirring was continued for 2 h at room temp. The solvent was removed in vacuo;

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the remaining brown oil was extracted with diethyl ether and subject to chromatography on silica gel (2 × 15 mL column). Elution with petroleum ether/diethyl ether (30:1) gave a first phase, which contained a small amount of $Cr(CO)_5CNCH_2Cl$. An orange fraction appeared thereafter, which could not be identified. More polar eluents were employed to elute the main products **13a**–**c** (**13a**, **13c**: petroleum ether/diethyl ether, 10:1–10:2; **13b**: petroleum ether/diethyl ether, 20:1–10:1) as mixtures of isomers. Thin layer chromatography showed the presence of practically equal amounts of *E* and *Z* isomers in each case. Separation of the isomers of **13a** and **13b** was finally successful through (four times) repeated chromatography followed by fractional recrystallization from CH_2Cl_2 at –25 °C. The separation of the isomers of **13c** was not attempted.

13a (mixture): Yellow crystals, m.p. 128 °C (dec.), yield 11 %. $C_{27}H_9ClCr_2N_2O_{11}$ (676.81): calcd. C 47.91, H 1.34, N 4.14; found C 48.02, H 1.58, N 4.44. **IR** (KBr) **isomer I**: $\tilde{\nu}$ = 3433 w [ν(NH)], 2114 m [ν(CN)], 2067 m, 2033 s, 1980 s, 1932 vs, br. [ν(CO)], 1660 m [ν(C=C)], 1452 s [ν(N–C–O)]; **isomer II**: $\tilde{\nu}$ = 3400 m [ν(NH)], 2113 m [ν(CN)], 2069 m, 2028 s, 2008 w, 1931 vs, br., 1873 s [ν(CO)], 1673 m [ν(C=C)], 1452 s [ν(N–C–O)]. **^{1}H NMR** ($CDCl_3$) (mixture): δ = 9.2 (NH), 7.1–7.8 (H_{ar}). **MS** (mixture): *m*/*z* (%) = 675 (11) $[M]^+$; 592 (2), 564 (14), 536 (11), 508 (18), 480 (3), 452 (3), 424 (13), 396 (22) $[M - nCO]^+$ (*n* = 3–10).

13b (isomer I): Yellow crystals, m.p. 159 °C (dec.), yield 22 %; (**isomer II**): yellow crystals, m.p. 140 °C (dec.), yield 19 %. $C_{17}H_7ClCr_2N_2O_{11}$ (554.68): calcd. C 36.81, H 1.27, N 5.05; found (**isomer I**) C 36.65, H 1.45, N 4.39; (**isomer II**) C 35.92, H 1.57, N 4.96. **IR** (KBr) **isomer I**: $\tilde{\nu}$ = 3427 w [ν(NH)], 2110 m [ν(CN)], 2065 m, 1985 w, 1926 vs, br. [ν(CO)], 1670 w [ν(C=C)], 1426 s [ν(N–C–O)]; **isomer II**: $\tilde{\nu}$ = 3385 w [ν(NH)], 2113 m [ν(CN)], 2067 m, 2027 w, 1936 vs, br. [ν(CO)], 1675 w [ν(C=C)], 1415 s [ν(N–C-O)]. **^{1}H NMR** (CD_2Cl_2) (mixture): δ = 9.95 (NH), 1.75 (CH_3). **MS** (**isomer I**): *m*/*z* (%) = 554 (29) $[M]^+$, 498 (2), 470 (4), 442 (18), 414 (100), 386 (38), 358 (5), 330 (5), 302 (20), 274 (20) $[M - nCO]^+$ (*n* = 2–10); 165 (26) $[CrL - COR_2 + H]^+$; (**isomer II**) *m*/*z* (int.): 554 (20) $[M]^+$; 470 (3), 442 (9), 414 (55), 386 (48), 358 (18), 330 (4), 302 (17), 274 (17) $[M - nCO]^+$ (*n* = 3–10); 165 (29) $[CrL - COMe_2 + H]^+$.

13c: Yellow crystals. **IR** (KBr) (mixture): $\tilde{\nu}$ = 3400 w, 3386 w [ν(NH)], 2115 w [ν(CN)], 2065 w, 2033 s, 1961 s, 1921 vs, br. [ν(CO)], 1666 w [ν(C=C)], 1433 s [ν(N–C–O)] **MS** (mixture): *m*/*z* (%) = 582 (25) $[M]^+$, 470 (17), 442 (100), 414 (34), 386 (6), 330 (15), 302 (17) $[M - nCO]^+$ (*n* = 4–7, 9,10); 165 (21) $[CrL - COEt_2 + H]^+$.

Synthesis of 14: Compound **1** (336 mg 1.0 mmol) and PhNCO (0.12 mL, 1.0 mmol) were dissolved in diethyl ether (20 mL). To this solution, a mixture of tris(dimethylamino)phosphane (0.37 mL, 2.0 mmol) in diethyl ether (5 mL) was added dropwise at room temp. The yellow solution turned dark red, and an oily precipitate formed mainly consisting of $[PPh_3Cl]Cl$. After stirring for another 2 h, the solution was siphoned off and the solvents were evaporated to dryness under high vacuum. The red resinous residue was redissolved in a small amount of ether and purified by column chromatography on neutral Al_2O_3 using diethyl ether/petroleum ether as eluent. The second fraction contained the product and was collected. Removal of the solvent left a light red powdery solid, which already was sufficiently pure. Yield 61 %, m.p. 93 °C. $C_{21}H_5ClCr_2N_3O_{11}$ (614.69): calcd. C 41.03, H 0.81, N 6.83; found C 42.15, H 1.27, N 7.01. **IR** (KBr): $\tilde{\nu}$ = 2125 s [ν(CN)], 2060 s, 2043 s, 1936 vs, br. [ν(CO)], 1682 m [ν(amide)], 1609 m [ν(C=C)], 1498 [ν_{as}(N–C–N)]. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.42 (m, 2 H, Ph), 7.24 (m, 2 H, Ph), 7.03 (m, 1 H, Ph). **^{13}C{^{1}H} NMR** ($CDCl_3$, 400 MHz): δ = 218.0 (CO_{trans}), 215.3 (CO_{cis}), 215.1 (CO_{trans}), 214.1 (CO_{cis}), 182.2 (CNR), 166.3 (>C=O), 132.5–125.8 (Ph), 115.6 (CCl).

X-ray Structure Determination of Complex 13a: In order to avoid hydrolysis of complex **12**, the brown oil obtained from **1**, fluorenone and $P(NMe_2)_3$, according to the general procedure for **13a**–**c**, was directly recrystallized from dichloromethane layered with diethyl ether at –25 °C, which means that chromatography was skipped. A piece measuring 0.42 × 0.38 × 0.20 mm was cut out from a cube-shaped crystal and mounted on fiberglass. All geometry and intensity data were collected on a STOE four circle diffractometer at –50 °C in the ω-2θ scan mode using Mo-K_α-radiation (λ = 0.71073 Å) and a graphite-monochromator. Neither absorption nor extinction corrections were carried out. The structure was solved by direct methods and developed using alternative cycles of full-matrix least-squares refinement and difference-Fourier synthesis (programs SHELXS-86, SHELXL-93 [27, 28]). With the exception of chromium and chlorine, some of the light atoms of the carbene-isocyanide bridging ligand (O1, N1, N2, C1, C2, C3), P and O2 of the side product, and Cl8 and Cl9 of the built-in CH_2Cl_2 solvent molecule, only an isotropic model was calculated. The molecular plot was produced with the ORTEP program [29].

$C_{27}H_9ClCr_2N_2O_{11}$ (676.82) + $O=P[N(CH_3)_2]_3$ (179.20) + CH_2Cl_2 (84.93), monoclinic, *C*2/*c* (Nr. 15), *a* = 39.854(18), *b* = 9.406(6), *c* = 23.858(12) Å, β = 108.02(4)°, *V* = 8507.48 Å^3, *Z* = 8, $\rho_{calcd.}$ = 1.469 Mg·m^{-3}, temperature = 223 K, 2θ range for data collection = 4.0–37.0°, reflections collected = 3426, observed reflections (≥3σ|F|) = 1541, parameters (refined) = 294, *R* = 10.1 %, R_w = 11.5 %, weighting scheme $w = 1/\sigma(F^2)$.

CCDC737354 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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