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Addition of diazoalkanes to alkyne(pentacarbonyl)–chromium and –tungsten — formation of 3H-pyrazole complexes

Mokhles M. Abd-Elzaher [1], Bernhard Weibert, Helmut Fischer *

Fachbereich Chemie, Universität Konstanz, Fach M727, 78457 Konstanz, Germany

Abstract

Photolysis of $[M(CO)_6]$ (M = Cr, W) in CH_2Cl_2 at -78 °C generates $[(CO)_5M(CH_2Cl_2)]$. Subsequent sequential reaction of $[(CO)_5M(CH_2Cl_2)]$ with terminal alkynes, $HC \equiv CR$ (R = COOMe, Ph, p-Tol), and diazoalkanes, $R^1(R^2)CN_2$ (R^1 = Me, Et, Ph; R_2 = Me, Et) affords 3H-pyrazole complexes, $[(CO)_5M–N=N–C(R)=C(H)–C(R^1)(R^2)]$. These complexes are derived from addition of diazoalkanes to alkyne complex intermediates, $[(CO)_5M(HC \equiv CR)]$. Their vinylidene tautomers, $[(CO)_5M=C=C(R)H]$, present in solution in equilibrium with the alkyne complexes, do not react. Likewise, isolable disubstituted vinylidene complexes, $[(CO)_5M=C=C(R')R^*]$, do not add diazoalkanes.
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1. Introduction

Until now only very few alkyne(pentacarbonyl) complexes have been isolated having terminal alkyne ligands. Only one complex, $[(CO)_5W(HC \equiv CPh)]$, has been characterized by an X-ray structural analysis [1]. However, such complexes can easily be generated and subsequently be used for a series of transformations. In solutions these complexes are present in a rapid equilibrium with their vinylidene tautomer. The equilibrium is far to the side of the alkyne form. Usually it is not possible to detect the vinylidene tautomer by spectroscopic means. Theoretical studies indicate that the alkyne/vinylidene isomerization proceeds in these d^6 complexes by an intramolecular process [2].

These complexes readily react for example (a) with alcohols to give carbene complexes [3], with (b) ynamines to form cyclobutenylidene complexes [1,4], and (c) with imines and carbodimides to form 2-azetidinylidene complexes [5,6] (Scheme 1).

$[(CO)_5W(HC \equiv CR)]$ can also be used as a pre-catalyst for the polymerization of terminal alkynes in hydrocarbon solutions. The polymerization of acetylene, $HC \equiv CH$, requires irradiation of the solutions to only initiate the reaction whereas for terminal alkynes continued irradiation is necessary [7]. The reaction of $[(CO)_5Cr(Et_2O)]$ with a stoichiometric amount of $HC \equiv C–COOMe$, however, afforded in addition to the alkyne complex $[(CO)_5Cr(HC \equiv C–COOMe)]$ two products derived from addition of the alkyne to the vinylidene complex tautomer, a cyclobutenylidene complex and a vinylvinylidene complex [8].

All of these reactions are best explained by assuming that the vinylidene tautomer is trapped by the substrate. We now report on reactions that proceed by addition of the substrate to the alkyne tautomer.
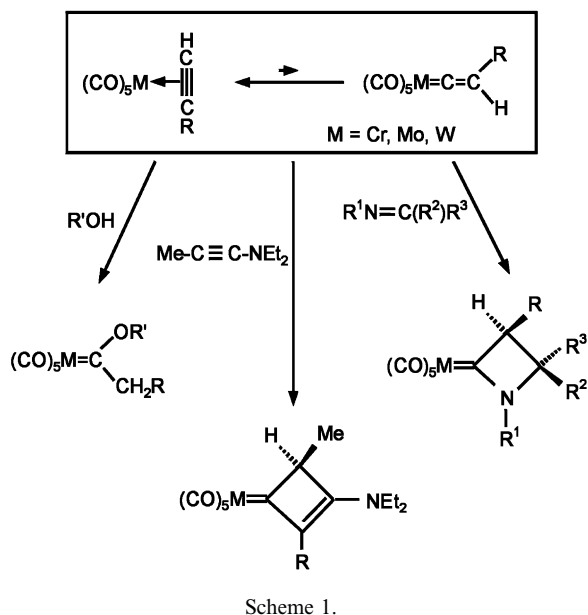
2. Results and discussion

The starting alkyne complexes were generated from the corresponding hexacarbonyl compounds. Irradiation of solutions of $[M(CO)_6]$ in CH_2Cl_2 at -78 °C afforded, through loss of one CO ligand, the pentacarbonyl complexes $[(CO)_5M(CH_2Cl_2)]$. Their formation

* Corresponding author. Tel.: +49-7531-882-783; fax: +49-7531-883-136.

E-mail address: helmut.fischer@uni-konstanz.de (H. Fischer).

[1] Present address: Inorganic Chemistry Department, National Research Centre, PO Box 12622 Dokki, Cairo, Egypt.
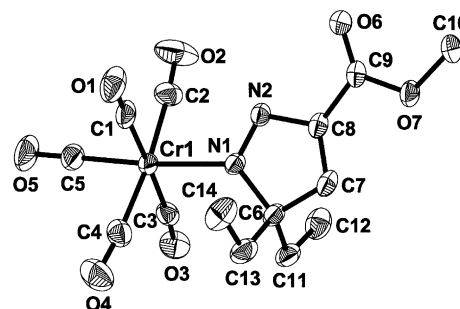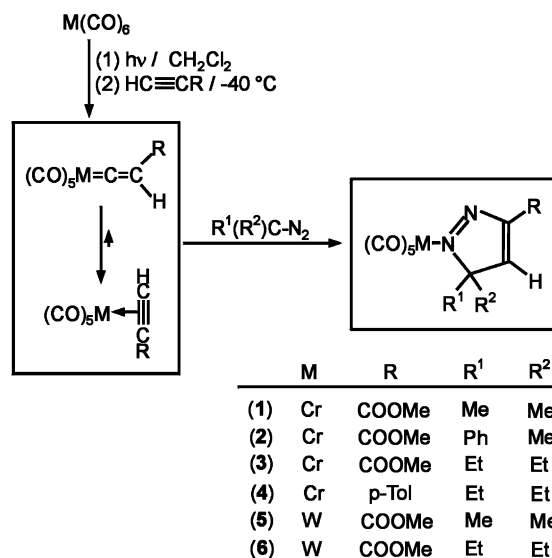
Scheme 1.

Fig. 1. Molecular structure of complex **3** in the crystal (hydrogen atoms omitted for clarity).

Table 1
Selected bond lengths (Å), bond and torsion angles (°) of complex **3**

Bond lengths			
Cr(1)−N(1)	2.138(2)	C(7)−C(8)	1.334(3)
N(1)−N(2)	1.272(2)	C(8)−C(9)	1.489(3)
N(1)−C(6)	1.509(2)	O(6)−C(9)	1.204(3)
N(2)−C(8)	1.438(3)	O(7)−C(9)	1.342(2)
C(6)−C(7)	1.485(3)	O(7)−C(10)	1.450(3)
Bond angles			
N(2)−N(1)−C(6)	110.81(16)	N(2)−C(8)−C(9)	119.08(17)
N(2)−N(1)−Cr(1)	119.13(12)	C(7)−C(8)−N(2)	110.26(18)
C(6)−N(1)−Cr(1)	130.05(13)	C(7)−C(8)−C(9)	130.63(19)
N(1)−N(2)−C(8)	109.26(16)	O(6)−C(9)−C(8)	125.18(19)
C(7)−C(6)−N(1)	101.57(16)	C(8)−C(7)−C(6)	108.10(18)
Torsion angles			
C(2)−Cr−N(1)−N(2)	33.6(2)	Cr−N(1)−C(6)−C(7)	179.9(1)
Cr−N(1)−N(2)−C(8)	179.8(1)	N(1)−N(2)−C(8)−C(7)	0.8(2)

could easily be followed by the changes of the ν(CO) absorptions in the IR spectra. Subsequent addition of two equivalents (relative to [M(CO)$_6$]) of terminal alkynes at −40 °C produced alkyne complexes generally in good yield. The formation of the alkyne complexes was verified by IR spectroscopy. Most of these complexes are thermally labile and readily decompose at room temperature. Therefore, they were not isolated but immediately used for the subsequent reactions after the volume of the solutions had been reduced in vacuo to a few milliliters. Two to three equivalents of diazoalkane, R^1(R^2)C−N$_2$, were added at −40 °C to the concentrated solutions. The reactions proceeded quickly and were complete within a few minutes. Chromatographic workup of the reaction mixture afforded the 3*H*-pyrazole complexes **1**–**6** (Scheme 2) in yields ranging from 56 to 74%.

The reaction of [(CO)$_5$Mo(CH$_2$Cl$_2$)] with HC≡C−COOMe and Et$_2$C−N$_2$ proceeded similarly, however, the resulting complex was very unstable. Therefore, it was not possible to isolate it in a pure form.

The compounds **1**–**6** are readily soluble in polar solvents such as dichloromethane or diethyl ether, but only poorly soluble in non-polar solvents. The complexes were characterized by their IR, ^{1}H-NMR, and ^{13}C-NMR spectra. The structure of **3** and **5** was additionally established by X-ray structural analyses.

The results of the X-ray analysis of **3** (Fig. 1, Table 1) shows that a 3*H*-pyrazole complex has been formed. The five-membered ring is bonded to chromium via the nitrogen atom adjacent to the sp^3 carbon atom. The pyrazole ring is planar. To avoid steric congestion, the ring is staggered with respect to the *cis* carbonyl ligands (torsion angle C(2)−Cr−N(1)−N(2) 33.6(2)°). The Cr−N(1) bond length (2.1384(18) Å) is similar to that

observed for other [(CO)$_5$CrL] complexes with an N(sp^2)-bonded *N*-heterocyclic ligand (L, e.g. 4-methyl-1,2,4-triazole-N1: 2.111(2) Å [9], 3-ethoxy-1*H*-isoindole-N: 2.134(3) Å [10], 4-methyl-1,2,3-selenadiazole-N: 2.114(6) Å [11]). (CO)$_5$Cr−N(sp^3) distances are usually

|	M	R	R^1	R^2
(1)	Cr	COOMe	Me	Me
(2)	Cr	COOMe	Ph	Me
(3)	Cr	COOMe	Et	Et
(4)	Cr	p-Tol	Et	Et
(5)	W	COOMe	Me	Me
(6)	W	COOMe	Et	Et

Scheme 2.

longer and are observed in the range 2.19 – 2.25 Å [12]. The N(1)–N(2) distance (1.272(2) Å) agrees very well the N(sp^2)=N(sp^2) bond length in (CO)$_5$Cr-coordinated 4-methyl-1,2,3-selenadiazole (1.272(1) Å [11]) and in 6-chloro 9,9-dimethyl 9H-imidazo(1,2-b)pyrazolo(4,3-d)pyridazine (1.265(8) Å [13]), but is significantly shorter than the N(sp^2)–N(sp^2) bond in [(CO)$_5$Cr(4-methyl-1,2,4-triazole)] (1.380(3) Å [9]). Bond lengths and angles in **5** deviate only sightly from those in **3**. Therefore, they are not discussed here.

The X-ray structural analyses of **3** and **5** and the spectroscopic data of **1**–**6** confirm that the new heterocyclic ligand is derived from the alkyne tautomer. From addition of diazoalkane to the vinylidene tautomer (as has been observed in all reactions with nucleophiles summarized in Scheme 1) the formation of isomeric 2-dihydropyrazolylidene complexes was to be expected. However, there is no spectroscopic indication for the formation of 2-dihydropyrazolylidene complexes. In accord with the conclusion is the observation that disubstituted pentacarbonyl(vinylidene) complexes did not react with diazoalkanes to give 2-dihydropyrazo-lylidene complexes. When solutions of [(CO)$_5$M=C=C(CMe$_3$)R] (M = Cr, W; R = Me, Et) were treated with phenyl diazomethane, phenyl diazoethane, diphenyl diazomethane, 4-methoxyphenyl diazomethane, or diazopentane using the same reaction conditions as previously applied (Scheme 2), after three hours the vinylidene complex was recovered unchanged. In addition, small amounts of its decomposition product, [M(CO)$_6$], and products derived from the thermal decomposition of the diazoalkane were isolated. 2-Dihydropyrazolylidene complexes could not be detected.

The formation of 3H-pyrazole complexes can be explained by two pathways (Scheme 3):

a) addition of the diazo compound to the coordinated alkyne followed by rearrangement or
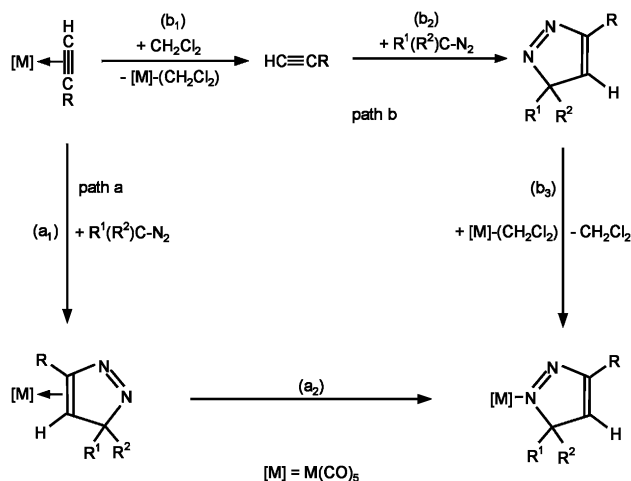
b) displacement of the coordinated alkyne by the solvent, 1,3-dipolar cycloaddition of the diazo compound to the non-coordinated alkyne to give the 3H-pyrazole followed by displacement of the coordinated solvent by 3H-pyrazole.

To distinguish between these two likely mechanisms several experiments with the system [(CO)$_5$Cr(CH$_2$Cl$_2$)]/HC≡C–COOMe/Et$_2$C–N$_2$ were carried out:

– The cycloaddition of Et$_2$C–N$_2$ to non-coordinated HC≡C–COOMe to form the 3H-pyrazole (step b$_2$) was faster than the overall reaction of Et$_2$C–N$_2$ with [(CO)$_5$Cr(HC≡C–COOMe)].

– The rate of displacement of coordinated CH$_2$Cl$_2$ by 3H-pyrazole (step b$_3$) was faster than the reaction of Et$_2$C–N$_2$ with [(CO)$_5$Cr(HC≡C–COOMe)] to form 3H-pyrazole complex.

– The rate of displacement of coordinated HC≡C–COOMe by nucleophiles, however, was considerably slower than the rate of formation of 3H-pyrazole complexes. P(C$_6$H$_4$Me-p)$_3$ (as a typical nucleophile) reacted only very slowly with [(CO)$_5$Cr(HC≡C–COOMe)]. From the reaction mixture only small amounts of stable [(CO)$_5$Cr(P(C$_6$H$_4$Me-p)$_3$)] were isolated. The major products were [Cr(CO)$_6$] and several organic products presumably derived from nucleophilic addition of P(C$_6$H$_4$Me-p)$_3$ to the coordinated alkyne and subsequent decomposition of the adduct.

From the significantly slower rate of step b$_1$ compared to the overall reactions of Scheme 2 it follows that path b can be excluded and that the 3H-pyrazole complexes are formed within the coordination sphere of the metal.

An alternative route involves reaction of excess alkyne with excess diazoalkane to form the 3H-pyrazole followed by displacement of coordinated alkyne by the 3H-pyrazole. This route, at least as the major pathway, is unlikely since displacement of coordinated alkynes by 3H-pyrazoles is considerably slower than the overall reaction (Scheme 2). Nevertheless, the formation of small amounts of the 3H-pyrazole complexes by this route cannot completely be excluded.

The rate of addition of diazoalkanes to the alkyne of the complexes [(CO)$_5$M(HC≡C–R)] depended on the substituent R. When HC≡C–COOMe was replaced by aryl-substituted alkynes the stability and also the reactivity towards nucleophiles decreased. When HC≡CPh was employed the displacement of the alkyne by nucleophiles already competed with 3H-pyrazole formation. Therefore, from the slow reaction of [(CO)$_5$Cr(HC≡C–Ph)] with Et$_2$C–N$_2$ three compounds were isolated (Scheme 4); the pyrazole complex **7**, small
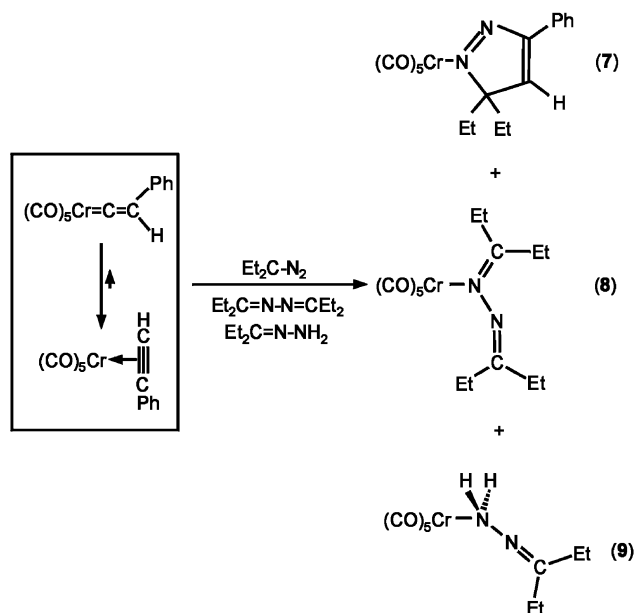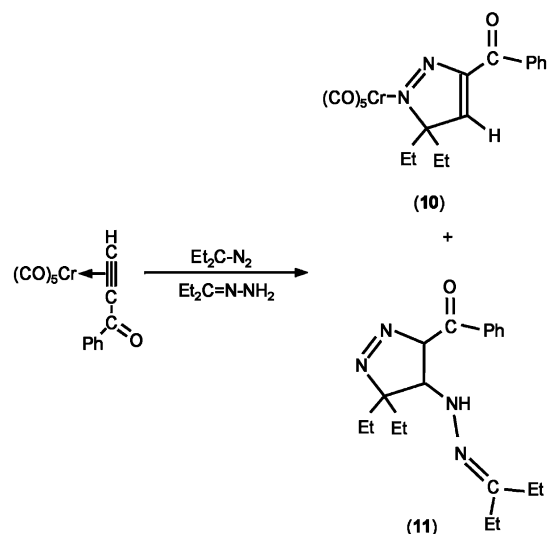
Scheme 3.

Scheme 4.

Scheme 5.

amounts of an azine complex (**8**), and the hydrazone complex (**9**).

The complexes **8** and **9** are formed by substitution of tetraethyl azine and 3-pentanone hydrazone, respectively, for coordinated phenylethyne. 3-Pentanone hydazone is an intermediate in the synthesis of 3-diazopentane from 3-pentanone, hydrazone, and HgO. Due to the modest stability of 3-diazopentane its purification is difficult and, therefore, it is usually accompanied by its precursor 3-pentanone hydrazone. Tetraethyl azine in turn is a well-known by-product in the synthesis of 3-diazopentane by oxidation of 3-pentanone hydrazone with HgO [14].

In contrast to the reaction of $[(CO)_5Cr(HC{\equiv}C{-}Ph)]$ with $Et_2C{-}N_2$ that of $[(CO)_5Cr(HC{\equiv}C{-}C(O)Ph)]$ was fast. However, the resulting $3H$-pyrazole complex **10** (Scheme 5) turned out to be too unstable for isolation. It quickly decomposed in solution even at $-30\ ^{\circ}C$ predominantly by decomplexation of the $3H$-pyrazole. The major product isolated from the reaction mixture by column chromatography was a green oil. From the molecular peak in its mass spectrum a combined mass of that of the $3H$-pyrazole and that of 3-pentanone hydrazone could be deduced. The ^{1}H-NMR spectrum exhibited in CDCl$_3$, in addition to resonances for one C$_6$H$_5$ substituent and four C$_2$H$_5$ groups, two doublets at $\delta = 4.55$ ($J = 3.0$ Hz) and 5.53 ($J = 2.8$ Hz) and a singulet at $\delta = 6.83$. The position of the singulet was concentration- and solvent-dependent. Its position in CDCl$_3$ varied between $\delta = 6.83$ and 7.16 depending on the concentration of the compound. In acetone-d_6 the singulet appeared at $\delta = 8.05$. The ^{13}C-NMR spectrum showed, in addition to peaks for the ethyl groups, the phenyl substituent, a C=O ($\delta = 188.8$) and a C=N

group ($\delta = 154.8$), three resonances at $\delta = 147.4$, 71.8, and 67.3. Based on these spectroscopic data we assign the structure shown in Scheme 5 to compound **11**. It is presumably formed by addition of 3-pentanone hydrazone present in solution as a by-product from the synthesis of 3-diazopentane to the $3H$-pyrazole.

Decomplexation of the $3H$-pyrazole in **1**–**6** could be achieved by addition of nucleophiles. For instance addition of [NBu$_4$]Br to solutions of 3 in CH$_2$Cl$_2$ and stirring the solutions for 48 h at ambient temperature afforded the $3H$-pyrazole after purification in 66% yield.

In summary, the reactions of the equilibrium alkyne(pentacarbonyl) complex/pentacarbonyl(vinylidene) complex strongly depends on the type of substrate. Whereas imines, ynamines, and alcohols preferentially react quickly with the vinylidene complex tautomer in the equilibrium, the products ($3H$-pyrazole complexes) of the reactions with diazoalkanes as typical 1,3-dipoles are derived from the alkyne complex tautomer.

3. Experimental

3.1. General

All operations were carried out under either nitrogen or argon by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium–benzophenone ketyl (THF, diethyl ether) or CaH$_2$ (pentane, dichloromethane) and were freshly distilled prior to use. The silica gel used for chromatography (J.T. Baker, silica gel for flash chromatography) was argon saturated. The yields refer to analytically pure compounds and were not optimized. 2-Acetone hydrazone [15], 2-diazopropane [16], 3-diazopentane [17], 1-phenyl diazoethane [18], bis-(p-dimethylaminophenyl) diazo-

methane [19] and benzoylacetylene [20] were prepared according to the literature procedures. Metal hexacarbonyls (Aldrich) and HgO, yellow (ACROS), and all other chemicals (Merck) were commercial products and were used without further purification. IR: FT-IR spectrophotometer (FTS70), Bio-Rad. All IR measurements were carried out at 298 K. ^{1}H- and ^{13}C-NMR spectra were recorded at room temperature on a Bruker AC 250. Chemical shifts are reported in ppm relative to internal TMS. For the numbering scheme see Fig. 1. MS: Finnigan MAT 312 (EI). Elemental analysis: CHN-analyser (CHN-O-RAPID) Heraeus. Photolysis reactions were carried out in a duran glass apparatus using a mercury high pressure lamp (TQ 150, Fa. Heraeus).

3.2. General procedure for the generation of the η^2-alkyne metal complexes

At $-78\ ^{\circ}$C, a solution of the metal hexacarbonyls, $[M(CO)_6]$ (2.84 mmol of $[W(CO)_6]$, 2.73 mmol of $[Cr(CO)_6]$, 3.79 mmol of $[Mo(CO)_6]$), in ca. 300 ml of dichloromethane was irradiated with a UV lamp while stirring. The progress of the photolysis was followed by IR-spectroscopy. After ca. 90 min the metal hexacarbonyls were converted into pentacarbonyl(dichloromethane)metal complexes. Two equivalents (based on the metal hexacarbonyls used) of the corresponding alkyne (RC≡CH; R = COOMe, Ph, *p*-tolyl, C(O)Ph) were added at $-78\ ^{\circ}$C with stirring to the freshly prepared solution of the $[(CO)_5M(CH_2Cl_2)]$ complexes. Stirring was continued for 10 min. The temperature was allowed to rise gradually from -78 to $-30\ ^{\circ}$C. The solution was concentrated at $-30\ ^{\circ}$C to a volume of ca. 10 ml. The η^2-alkyne(pentacarbonyl)metal complexes $[(CO)_5M(HC≡CR)]$ (M = Cr: R = COOMe, C(O)Me, Ph, *p*-Tol; M = Mo: R = COOMe; M = W: R = COOMe, Ph) were identified by comparison of their IR spectra with published data [1,5,6]. The solutions containing the η^2-alkyne(pentacarbonyl)metal complexes were immediately used for the subsequent reactions.

3.3. Reaction of η^2-alkyne(pentacarbonyl)metal complexes with diazo compounds

At $-30\ ^{\circ}$C, the diazo compound (two equivalents, relative to $[M(CO)_6]$) was added to the concentrated solutions of the alkyne complexes. The progress of the reaction was monitored by IR spectroscopy. When the starting alkyne complexes could not be detected any more, the solvent was removed in vacuo. A brown oily product was obtained. Then, the reaction products were chromatographed at $-50\ ^{\circ}$C on silica gel or neutral Al_2O_3. Elution with pentane gave first $[M(CO)_6]$ and subsequently with pentane/dichloromethane a red band containing 3*H*-pyrazole complexes.

3.3.1. Pentacarbonyl(3,3-dimethyl-5-methoxycarbonyl-3H-pyrazole-N2)chromium(0) (1)

Elution of the complex with pentane+CH_2Cl_2 (1:1). Yield: 0.75 g (72% relative to $[Cr(CO)_6]$). M.p. 76 $^{\circ}$C. IR (pentane, 298 K, cm^{-1}) $\nu(CO)$ = 2071 m, 1954 vs, 1943 s, 1921 s, 1742 m. ^{1}H-NMR (CD$_3$C(O)CD$_3$): δ = 8.32 (s, 1H, C7-H), 3.87 (s, 3H, OMe), 1.62 (s, 6H, C6–CH$_3$). ^{13}C-NMR (CD$_3$C(O)CD$_3$): δ = 222.2 (*trans* CO), 214.9 (*cis* CO), 160.5 (C9), 158.3 (C7), 147.8 (C8), 99.4 (C6), 52.7 (OCH$_3$), 22.4 (C*C*H$_3$). MS, *m/z* (%): 346 (1.0) [M$^+$], 318 (3) [M$^+$−CO], 234 (6) [M$^+$−4CO], 206 (29) [M$^+$−5CO], 147 (27.3) [M$^+$−5CO−C(O)OMe]. Anal. Found: C, 41.95; H, 2.99; N, 7.84. Calc. for C$_{12}$H$_{10}$N$_2$O$_7$Cr (346.2): C, 41.63; H, 2.91; N, 8.09%.

3.3.2. Pentacarbonyl(3-methyl-3-phenyl-5-methoxycarbonyl-3H-pyrazole-N2)chromium(0) (2)

Elution of the complex with pentane+CH_2Cl_2 (1:1). Yield: 0.69 g (56% relative to $[Cr(CO)_6]$), two isomers, **2a** and **2b** (ratio **2a**:**2b** = 1:1.6). M.p. 70 $^{\circ}$C. IR (pentane, 298 K, cm^{-1}) $\nu(CO)$ = 2070 m, 2066 m, 1995 m, 1955 vs, 1950 s, 1932 s, 1743 m. ^{1}H-NMR (CD$_3$C(O)CD$_3$): δ = 8.33 (s, C7–H, **2a**), 8.22 (s, C7–H, **2b**), 7.5–7.2 (m, aryl), 3.78 (s, OMe, **2b**), 3.69 (s, OMe, **2a**), 2.14 (s, Me, **2a**), 1.98 (s, Me, **2b**). ^{13}C-NMR (CD$_3$C(O)CD$_3$): δ = 222.3 (*trans* CO, **2a**), 221.7 (*trans* CO, **2b**), 214.0 (*cis* CO, **2b**), 213.8 (*cis* CO, **2a**), 160.5 (C9, **2b**), 159.8 (C9, **2a**), 152.2 (C7), 150.0 (C8), 146.5, 131.1, 129.4, 129.2, 128.9, 128.7, 128.4, 126.1 (m, aryl), 98.4 (C6), 52.0 (OCH$_3$, **2b**), 51.8 (OCH$_3$, **2a**), 22.7 (C*C*H$_3$, **2a**), 19.9 (C*C*H$_3$, **2b**). MS, *m/z* (%): 408 (13) [M$^+$], 352 (5.6) [M$^+$−2CO], 324 (8.1) [M$^+$−3CO], 296 (4.3) [M$^+$−4CO], 268 (100) [M$^+$−5CO]. Anal. Found: C, 50.95; H, 3.58; N, 6.88. Calc. for C$_{17}$H$_{12}$N$_2$O$_7$Cr × 0.15 pentane (408.3+10.8): C, 50.82; H, 3.29; N, 6.68%.

3.3.3. Pentacarbonyl(3,3-diethyl-5-methoxycarbonyl-3H-pyrazole-N2)chromium(0) (3)

Elution of the complex with pentane+CH_2Cl_2 (1:9). Yield: 0.85 g (76% relative to $[Cr(CO)_6]$). M.p. 73 $^{\circ}$C. IR (pentane, 298 K, cm^{-1}) $\nu(CO)$ = 2069 m, 1997 m, 1950 vs, 1942 s, 1922 s, 1745 m. ^{1}H-NMR (CD$_3$C(O)CD$_3$): δ = 8.23 (s, 1H, C7), 3.91 (s, 3H, OMe), 2.45 (m, 2H, CH$_2$), 2.28 (m, 2H, CH$_2$), 0.56 (t, *J* = 7.4 Hz, 6H, CH$_3$). ^{13}C-NMR (CD$_3$C(O)CD$_3$): δ = 222.2 (*trans* CO), 214.9 (*cis* CO), 160.3 (C9), 156.6 (C7), 150.2 (C8), 108.3 (C6), 52.8 (OCH$_3$), 31.0 (CH$_2$), 9.0 (C*C*H$_3$). MS, *m/z* (%): 374 (2.3) [M$^+$], 262 (21.4) [M$^+$−4CO], 234 (100) [M$^+$−5CO], 175 (27.3) [M$^+$−5CO−C(O)OMe]. C$_{14}$H$_{14}$N$_2$O$_7$Cr (374.3).

3.3.4. Pentacarbonyl(3,3-diethyl-5-p-tolyl-3H-pyrazole-N2)chromium(0) (4)

Elution of the complex with pentane+CH_2Cl_2 (1:9). Yield: 0.54 g (44% relative to $[Cr(CO)_6]$). M.p. 96 $^{\circ}$C. IR (pentane, 298 K, cm^{-1}) $\nu(CO)$ = 2068 m, 1947 vs, 1940

s, 1920 s. ^{1}H-NMR (CDCl$_3$): $\delta = 7.85$ (d, $J = 7.6$ Hz, 2H, aryl), 7.28 (d, $J = 7.6$ Hz, 2H, aryl), 6.99 (s, 1H, C7–H), 2.41 (s, 3H, aryl–CH$_3$), 2.21 (m, 4H, CH$_2$), 0.60 (t, $J = 6.8$ Hz, 6H, CH$_3$). ^{13}C-NMR (CDCl$_3$): $\delta = 221.6$ (*trans* CO), 214.3 (*cis* CO), 156.6 (C8), 136.2 (C7), 140.0, 130.1, 129.8, 126.6 (aryl), 106.2 (C6), 30.7 (CH$_2$), 21.4 (aryl-CH$_3$), 8.9 (CH$_3$). MS, *m/z* (%): 406 (7.2) [M$^+$], 350 (3.5) [M$^+ - 2$CO], 266 (73) [M$^+ - 5$CO]. Anal. Found: C, 56.14; H, 4.70; N, 6.77. Calc. for C$_{19}$H$_{18}$N$_2$O$_5$Cr (406.4): C, 56.16; H, 4.46; N, 6.89%.

3.3.5. Pentacarbonyl(3,3-dimethyl-5-methoxycarbonyl-3H-pyrazole-N2)tungsten(0) (5)

Elution of the complex with pentane+CH$_2$Cl$_2$ (1:9). Yield: 0.87 g (64% relative to [W(CO)$_6$]). M.p. 82 °C. IR (pentane, 298 K, cm^{-1}) v(CO) = 2075 m, 1990 m, 1948 vs, 1943 s, 1922 s, 1741 m. ^{1}H-NMR (CD$_3$C(O)CD$_3$): $\delta = 8.39$ (s, 1H, C7), 3.90 (s, 3H, O–CH$_3$), 1.64 (s, 6H, CH$_3$). MS, *m/z* (%): 478 (6) [M$^+$], 394 (9) [M$^+ - 3$CO], 338 (20) [M$^+ - 5$CO], 279 (18) [M$^+ - 5$CO–C(O)OMe]. Anal. Found: C, 31.12; H, 2.42; N, 6.17. Calc. for C$_{12}$H$_{10}$N$_2$O$_7$W × 0.1 pentane (478.1+7.2): C, 30.91; H, 2.31; N, 5.77%.

3.3.6. Pentacarbonyl(3,3-diethyl-5-methoxycarbonyl-3H-pyrazole-N2)tungsten(0) (6)

Elution of the complex with pentane+CH$_2$Cl$_2$ (1:9). Yield: 0.74 g (52% relative to [W(CO)$_6$]). M.p. 86 °C (dec.). IR (pentane, 298 K, cm^{-1}) v(CO) = 2074 m, 1990 w, 1945 vs, 1941 vs, 1921 m, 1747 m. ^{1}H-NMR (CD$_3$C(O)CD$_3$): $\delta = 8.36$ (s, 1H, C7–H), 3.94 (s, 3H, O–CH$_3$), 2.5–2.2 (m, 4H, CH$_2$), 0.58 (t, $J = 7.4$ Hz, 6H, CH$_3$). ^{13}C-NMR (CD$_3$C(O)CD$_3$): $\delta = 201.9$ (*trans* CO), 197.5 (*cis* CO), 158.4 (C9), 154.4 (C7), 152.8 (C8), 107.0 (C6), 52.0 (OCH$_3$), 31.0 (CH$_2$), 8.1 (CCH$_3$). MS: *m/z* (%): 506 (28.5) [M$^+$], 450 (56.4) [M$^+ - 2$CO], 422 (45) [M$^+ - 3$CO], 366 (100) [M$^+ - 5$CO], 337 (36) [M$^+ - 5$CO–Et]. Anal. Found: C, 34.74; H, 3.46; N, 5.30. Calc. for C$_{14}$H$_{14}$N$_2$O$_7$W × 0.25 pentane (506.1+18.0): C, 34.91; H, 3.25; N, 5.34%.

3.4. Reaction of η^2-pentacarbonyl(phenylethyne)-chromium with 3-diazopentane: pentacarbonyl(3,3-diethyl-5-phenyl-3H-pyrazole-N2)chromium(0) (7), pentacarbonyl(tetraethyl azine)chromium(0) (8), and pentacarbonyl(diethyl ketonehydrazone)chromium(0) (9)

At −30 °C, two equivalents of 3-diazopentane (relative to [Cr(CO)$_6$]) was added to the concentrated solutions of [(CO)$_5$Cr(HC≡C–Ph)]. The progress of the reaction was monitored by IR spectroscopy. After ca. 45 min, the solvent was removed in vacuo and the residue was chromatographed at −50 °C on silica gel. Elution with pentane gave first [Cr(CO)$_6$] and then with pentane+CH$_2$Cl$_2$ (9:1) a red band containing the 3H-

pyrazole complexes (7). Next, with pentane+CH$_2$Cl$_2$ (7:3) a violet–green band was eluted containing the hydrazone complex 8. Finally, the azine complex 9 was eluted with pentane+CH$_2$Cl$_2$ (1:1) as a slight green band.

7: yield: 0.49 g (42% relative to [Cr(CO)$_6$]). M.p. 78 °C. IR (pentane, 298 K, cm^{-1}) v(CO) = 2068 m, 1993 m, 1948 vs, 1940 s, 1921 s. ^{1}H-NMR (CDCl$_3$): $\delta = 7.96$ (m, 2H, aryl), 7.48 (m, 3H, aryl), 7.07 (s, 1H, C7–H), 2.22 (m, 4H, CH$_2$), 0.62 (t, $J = 6.4$ Hz, 6H, CH$_3$). ^{13}C-NMR (CDCl$_3$): $\delta = 221.6$ (*trans* CO), 214.3 (*cis* CO), 156.5 (C8), 137.2 (C7), 129.8, 129.4, 129.1, 126.7 (aryl), 106.4 (C6), 30.8 (CH$_2$), 9.0 (CH$_3$). MS, *m/z* (%): 392 (7.1) [M$^+$], 364 (3.4) [M$^+ - $CO], 336 (8.7) [M$^+ - 2$CO], 308 (4.5) [M$^+ - 3$CO], 280 (19.4) M$^+ - 4$CO], 252 (59.8) [M$^+ - 5$CO]. Anal. Found: C, 55.38; H, 4.09; N; 6.98. Calc. for C$_{18}$H$_{16}$CrN$_2$O$_5$ (392.3):C, 55.11; H, 4.11; N 7.14%.

8: yield: 0.10 g (9.0% relative to [Cr(CO)$_6$]). Green oil at room temperature (r.t.). IR (pentane, 298 K, cm^{-1}) v(CO) = 2069 m, 1934 vs, 1900 s. ^{1}H-NMR (CDCl$_3$): $\delta = 2.31$ (q, 4H, $J = 7.2$ Hz, CH$_2$), 2.27 (q, 4H, $J = 7.4$ Hz, CH$_2$), 1.14 (t, 4H, $J = 7.3$ Hz, CH$_3$), 0.99 (t, 4H, $J = 7.5$ Hz, CH$_3$). ^{13}C-NMR (CDCl$_3$): $\delta = 221.8$ (*trans* CO), 214.2 (*cis* CO), 166.1 (2 C=N), 28.9, 23.4 (CH$_2$), 10.5, 10.1(CH$_3$). MS, *m/z* (%): 360 (8.3) [M$^+$], 248 (22.4) [M$^+ - 4$CO], 220 (100) [M$^+ - 5$CO], 163 (37.7) [M$^+ - 5$CO–2Et]. C$_{15}$H$_{20}$CrN$_2$O$_5$ (360.1).

9: yield: 0.25 g (21% relative to [Cr(CO)$_6$]). M.p. 106 °C. IR (pentane, 298 K, cm^{-1}) v(CO) = 2070 m, 1937 vs, 1916sh. ^{1}H-NMR (CD$_3$C(O)CD$_3$): $\delta = 6.26$ (s, 2H, NH$_2$), 2.41 (q, $J = 7.6$ Hz, CH$_2$), 2.27 (q, $J = 7.3$ Hz, CH$_2$), 1.13 (t, $J = 7.6$ Hz, CH$_3$), 1.07 (t, $J = 7.6$ Hz, CH$_3$). ^{13}C-NMR (CD$_3$C(O)CD$_3$): $\delta = 221.8$ (*trans* CO), 215.7 (*cis* CO), 166.2 (C=N), 21.4 (CH$_2$), 10.8, 10.6 (CH$_3$). MS, *m/z* (%): 292 (5.27) [M$^+$], 264 (16.8) [M$^+ - $CO], 208 (4.8) [M$^+ - 3$CO], 180 (36.3) [M$^+ - 4$CO], 152 (75.0) [M$^+ - 5$CO], 123 (100) [M$^+ - 5$CO–Et]. Anal. Found: C, 40.86; H, 4.18; N, 9.50. Calc. for C$_{10}$H$_{12}$CrN$_2$O$_5$ (292.2): C, 41.10; H, 4.14; N, 9.59%.

3.5. Reaction of η^2-benzoylethyne(pentacarbonyl)-chromium with 3-diazopentane: pentacarbonyl(3,3-diethyl-5(benzoyl-3H-pyrazole-N2)chromium(0) (10) and 3,3-diethyl-4-(N-pentane hydrazone)-5-benzoylpyrazoline (11)

At −30 °C, two equivalents of 3-diazopentane (relative to [Cr(CO)$_6$]) were added to the concentrated solutions of [(CO)$_5$Cr(HC≡C–C(O)Ph)]. After ca. 15 min, the solvent was removed in vacuo and the residue was chromatographed at −50 °C on silica gel. Elution with pentane gave first [Cr(CO)$_6$], and then with pentane+CH$_2$Cl$_2$ (9:1) a red band containing the 3H-pyrazole complexes 10. Finally, with pentane+CH$_2$Cl$_2$

(7:3) a olive-green band was eluted containing compound **11**. Complex **10** was unstable and rapidly decomposed at room temp. It was therefore identified by the similarity of its IR spectrum (pentane, 298 K, cm^{-1}: ν(CO) = 2065 m, 1987 m, 1942 vs, 1937 s, 1913 s, 1723 m) with that of the other 3*H*-pyrazole complexes.

11: yield: 0.53 g (54% relative to [Cr(CO)$_6$]). Green oil at r.t. ^{1}H-NMR (CDCl$_3$): δ = 8.01 (d, J = 7.2 Hz, 2H, aryl), 7.42 (m, 3H, aryl), 6.83 (s, 1H, NH), 5.53 (d, J = 2.8 Hz, 1H, C$_5$H), 4.55 (d, J = 3.0 Hz, 1H, C$_4$H), 2.09 (q, J = 7.5 Hz, 4H, CH$_2$), 1.78 (q, J = 7.4 Hz, 2H, CH$_2$), 1.59 (q, J = 7.7 Hz, 2H, CH$_2$), 1.02 (t, J = 7.6 Hz, 3H, Me), 0.95 (t, J = 7.6 Hz, 6H, Me), 0.90 (t, 6 J = 7.4 Hz, 3H, Me). ^{13}C-NMR (CDCl$_3$): δ = 188.8 (C=O), 154.8 (N=C(sp^2)), 147.4 (CEt$_2$), 137.8, 131.6, 129.6, 127.7 (aryl), 71.8 (C5), 67.3 (C4), 29.2, (2 CH$_2$), 24.0 (CH$_2$), 21.4 (CH$_2$), 10.7, 9.3, 8.6, 7.6 (CH$_3$). MS, m/z (%): 328 (13.7) [M$^+$], 244 (22.5) [M$^+$−2Et−C−N], 201 (36) [M$^+$−3Et−C−2N], 172 (13.5) [M$^+$−4Et−C−2N]. Anal. Found: C, 68.06; H, 8.44; N, 16.43. Calc. for C$_{19}$H$_{28}$N$_4$O × 0.1 CH$_2$Cl$_2$: (328.5+9.7): C, 68.02; H, 8.37; N, 16.62%.

3.6. Decomplexation of the 3H-pyrazole ligand in pentacarbonyl(3,3-diethyl-5-methoxycarbonyl-3H-pyrazole-N2)chromium(0) (3)

[Bu$_4$N]Br (1.4 g, 4.3 mmol) was added to a solution of **3** (0.70 g). The solution was stirred for 48 h at r.t. Gradually, the red color and the ν(CO) absorptions in the IR spectrum disappeared. The precipitate was filtered over kieselgur and washed with cold pentane. The solvent was evaporated to afford the 3*H*-pyrazole. Yield: 0.46 g (66%). M.p. 95 °C. IR (pentane, 298 K, cm^{-1}) ν(CO) = 1758 m. ^{1}H-NMR (CDCl$_3$): δ = 7.68 (s, 1H, CH), 4.02 (s, 3H, OCH$_3$), 2.2–2.0 (m, 4H, CH$_2$), 0.68 (t, 6H, CH$_3$). ^{13}C-NMR (CDCl$_3$): δ = 152.8 (CO), 148.4 (C6), 133.9 (C7), 107.2 (C8), 52.5 (OCH$_3$), 27.0 (CH$_2$), 10.4 (CCH$_3$). MS (FAB), m/z (%): 183 (100) [M$^+$+H], 152 (70) [M$^+$+H−OMe]. Anal. Found: C, 59.11; H, 7.72; N, 15.15. Calc. for C$_9$H$_{14}$N$_2$O$_2$ (182.2): C, 59.32; H, 7.74; N, 15.37%.

The compound 3,3-diethyl-5-methoxycarbonyl-3*H*-pyrazole was independently prepared from 2.0 g (24 mmol) of methyl propynoate in 5 ml of CH$_2$Cl$_2$ and one equivalent of 3-diazopentane in 15 ml of diethyl ether. After mixing the solutions at −30 °C, the red color of 3-diazopentane disappeared within 1 min. The reaction mixture was warmed to r.t. The solvent was removed in vacuo and the residue was recrystallized from diethyl ether. Yield: 3.42 g (79%). M.p. 95 °C. IR (pentane, 298 K): ν(CO) = 1758 m. ^{1}H-NMR (CDCl$_3$): δ = 7.65 (s, 1H, CH), 4.00 (s, 3H, OCH$_3$), 2.14 (m, 4H, CH$_2$), 0.68 (t, 6H, CCH$_3$). ^{13}C-NMR (CDCl$_3$): δ = 152.8 (CO), 148.4 (C5), 133.9 (C4), 107.2 (C3), 52.5 (OCH$_3$), 27.0 (CH$_2$), 10.4 (CCH$_3$). MS, m/z%): 182 (6.1) [M$^+$], 167 (8.0)

[M$^+$−Me], 138 (57.5) [M$^+$−Me−Et], 110 (22.9) [M$^+$−Me−2Et], 94 (100) [M$^+$−Me−2 Et−O]. Anal. Found: C, 59.20; H, 7.70; N, 15.30. Calc. For C$_9$H$_{14}$N$_2$O$_2$ (182.2): C, 59.32; H, 7.74; N, 15.37%.

3.7. X-ray structural analyses of 3

C$_{14}$H$_{14}$CrN$_2$O$_7$, molecular mass (374.27), crystal size 0.4 × 0.4 × 0.4 mm^3 (obtained by recrystallization from dichloromethane+pentane (1:9)); crystal system monoclinic, space group $P2_1/c$, a = 7.224(2) Å, b = 13.436(4) Å, c = 17.514(5) Å, β = 97.04(2)°; V = 1687.2(9) Å^3, Z = 4, D_{calc} = 1.473 g cm^{-3}, absorption coefficient 0.715 mm^{-1}, F(000) 768; scan type: adaptive ω, Θ range 2.34–27.0°, 4943 independent reflections, 3691 reflection with $I > 2\sigma(I)$; 217 refined parameters; R_1 = 0.0390, wR_2 = 0.0941. Largest difference peak (hole): + 0.315 e Å^{-3} (−0.487 e Å^{-3}). The measurements were performed at −85 °C with a crystal mounted on a glass fibre on a Bruker P4 diffractometer (graphite monochromator, Mo–K$_\alpha$ radiation, λ = 0.71073 Å). The structures was solved by direct methods using the SHELXTL-97 program package [21]. The positions of the hydrogen atoms were calculated in ideal geometry and refined in the 'riding model'. All other atoms were refined anisotropically.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 194293 and 194294 for compounds **3** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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