Organometallics 1993, 12, 3241-3248

Reactions of Chromio, Tungstenio, and Platinio Nitrile Ylides with Aryldiazonium Salts. Triazolin-5-ylidene Complexes vs Cleavage of the N$\equiv$N(Ar) Bond and Formation of *N*-Cyanamidines[1]

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Received March 29, 1993

The metallo nitrile ylides [M]CNCHR$^-$ ([M] = W(CO)$_5$, R = Tos; [M] = [Pt(Cl)(PPh$_3$)$_2$]$^+$, R = CO$_2$Et) have been regenerated by deprotonation with LiBu^n or NEt$_3$ of the metal-coordinated α-CH-acidic isocyanides TOSMIC and ethyl isocyanoacetate and reacted regiospecifically with the aryldiazonium salts [4-XC$_6$H$_4$N$_2$]BF$_4$ (X = H, Cl, Me, NO$_2$, NMe$_2$), [4-MeOC$_6$H$_4$N$_2$]PF$_6$, and [2,4,6-Me$_3$C$_6$H$_2$N$_2$]BF$_4$ to give the carbenoid and carbanionic 1,2,4-triazoles **1**–**10**. In the case of the nitrile ylides [M{CNCHCO$_2$Et}(CO)$_5$]$^-$ (M = Cr, W), however, two isomeric products, 1,2,4-triazolin-5-ylidene (**11a**–**15a**) and *N*-cyanamidine complexes (**11b**–**15b**) were obtained. The latter can formally be described as products of insertion of isocyanide into the N$\equiv$N triple bond of the diazonium component. The structural assignments are made on the basis of IR, NMR (^{1}H, ^{13}C), and mass spectroscopy data as well as X-ray structure analyses of Cr(CO)$_5$-$\{\overline{\mathrm{CN(H)C(CO_2Et)NN}}\mathrm{Ph}\}$ (**11a**) and Cr(CO)$_5${N$\equiv$CN$=$C(CO$_2$Et)N(H)-C$_6$H$_4$Cl-4} (**12b**).

Introduction

In several papers we and others have shown that metal-coordinated α-deprotonated isocyanides are genuine 1,3-dipoles of the type of nitrile ylides which react with various dipolarophiles by [3 + 2] cycloadditions to give C-metalated five-membered heterocycles. A considerable number of pyrroles, pyrrolines, imidazoles, oxazoles, oxazolines, and thiazoles carrying metal complex substituents have been obtained in this way.[2]

"Free" 1,2,4-triazoles are compounds of pharmaceutical interest.[3] Several synthetic routes to this class of heterocycles have therefore been devised.[4] Occasionally, diazonium salts have been used as starting materials, for instance, in the formation of 1,2,4-triazoles from *N*-acetyl-2-cyanoglycine[5] and in cycloadditions with α-deprotonated ethyl isocyanoacetate[6] or tosylmethyl isocyanide.[7]

For 1,2,4-triazoles, an extensive coordination chemistry has also developed in the past few decades; many classical N-bonded metal complexes have been studied by Haasnoot, Vos, and others with regard to unusual structural, magnetic, and photochemical properties, including bioinorganic areas.[8]

In the following we report on reactions of metallo nitrile ylides with aryldiazonium salts which we expected to afford the first "organometallic" 1,2,4-triazoles in the form of triazolin-5-ylidene and/or triazol-5-ato complexes.

Results and Discussion

Reactions of the Tungstenio Nitrile Ylide [(OC)$_5$W—C$\equiv$N—CHTos]$^-$. The metallo nitrile ylide is generated by deprotonation of W(CO)$_5$TOSMIC[9] with LiBu^n at −78 °C, and an equimolar amount of aryldiazonium tetrafluoroborate is added. After several hours at this temperature, the reaction mixture is slowly warmed to room temperature. Workup, including chromatography, finally leads to fairly air-stable pale yellow to yellow microcrystalline products (**1**–**5**) in satisfactory yields (eq 1).

The substitution pattern of the diazonium salt appears to have little or no influence on the course of the reaction, which is about as efficient with the strongly electrophilic 4-O$_2$NC$_6$H$_4$N$_2^+$ as it is with 4-Me$_2$NC$_6$H$_4$N$_2^+$. In the IR spectra, the intense ν(C$\equiv$N) bands at ~2150 cm^{-1} have disappeared, and some new bands have emerged in the

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[9] TOSMIC: Tosylmethyl isocyanide.

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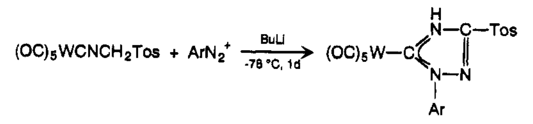


(1)

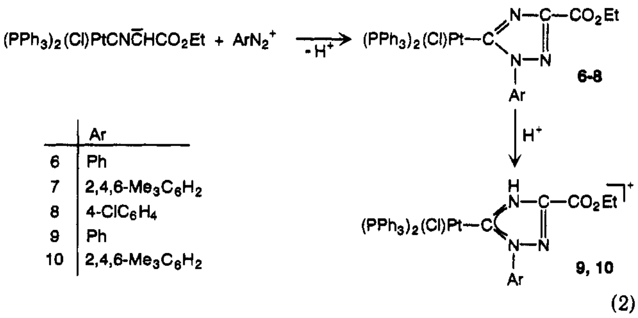
	Ar
1	Ph
2	4-ClC$_6$H$_4$
3	4-MeOC$_6$H$_4$
4	4-O$_2$NC$_6$H$_4$
5	4-Me$_2$NC$_6$H$_4$

region between 1600 and 1200 cm^{-1} which to some extent are indicative of the newly formed heterocyclic ligands. The ν(CO) absorptions as a whole have moved to markedly lower wavenumbers, an expected consequence of replacing an isocyanide ligand by a much better σ-donating *N,N'*-carbene. Medium to strong absorption bands around 3300 cm^{-1} are due to ν(N—H) and perhaps are most characteristic for the new complexes (Table I).

For each compound, the molecular peak is detected in the mass spectra, and it is accompanied by the mass lines of successive loss of carbonyl groups. In all cases, also the peak of the free heterocycle is observed (Table I).

In the ^{1}H NMR spectra, the signal at lowest field disappears on addition of D$_2$O, allowing its unequivocal assignment to the NH proton. The ^{13}C resonances of the carbene carbon atoms (C^5) are found at $\sim$185 ppm, which is in the normal range for *di*heteroatom-stabilized carbene complexes (Table II).[2g,10]

Reactions of the Platinio Nitrile Ylide [(PPh$_3$)$_2$(Cl)Pt—C≡N—CHCO$_2$Et]. There exists a correlation between the reactivity of coordinated isocyanides toward nucleophiles and the IR frequency of the CN group,[10–12] which at platinum(II) is up to 100 wavenumbers higher than at carbonylchromium(0) and -tungsten(0) centers. For corresponding reactions of *trans*-[Pt(Cl)(CNCH$_2$CO$_2$Et)(PPh$_3$)$_2$]BF$_4$ with diazonium ions to occur, it is thus sufficient to generate a low stationary concentration of the platinio nitrile ylide *trans*-[(PPh$_3$)$_2$(Cl)Pt—C≡N—CHCO$_2$Et] using triethylamine as a base; the reactions are then completed within a few hours. Note that, in the complexes **6–8**, the heterocyclic ligand is a carbanion. Protonation with ethereal HBF$_4$ gives the cationic carbene complexes **9** and **10** (eq 2).



	Ar
6	Ph
7	2,4,6-Me$_3$C$_6$H$_2$
8	4-ClC$_6$H$_4$
9	Ph
10	2,4,6-Me$_3$C$_6$H$_2$

(2)

The neutral complexes **6–8** give rise to molecular peaks in the mass spectra. Between the carbanionic and the carbene species minor differences exist in the ν(Pt—Cl) stretching frequencies, which run to $\sim$320 cm^{-1} for **9** and **10** as compared to $\sim$305 cm^{-1} for **6–8**. In the ^{13}C NMR spectra, in contrast, the carbene carbon signal (**9**: δ 145.7 ppm) is at markedly higher field than the platinum-bonded carbon atoms in **6** and **7** (δ $\sim$160.5 ppm). Due to the magnetic nonequivalence of the two phosphorus atoms and extensive ^{13}C/^{31}P coupling, the aromatic region is complex. Thus, only combined coupling constants are given (Experimental Section).[13]

Reactions of the Chromio and Tungstenio Nitrile Ylides [(OC)$_5$M—C≡N—CHCO$_2$Et]$^-$. The reactions of [(OC)$_5$M—C≡N—CHCO$_2$Et]$^-$ (M = Cr, W) with the diazonium salts [PhN$_2$]BF$_4$, [4-ClC$_6$H$_4$N$_2$]BF$_4$, and [4-MeC$_6$H$_4$N$_2$]BF$_4$—with 4-Me$_2$NC$_6$H$_4$N$_2^+$ no reaction occurred, and with 4-O$_2$NC$_6$H$_4$N$_2^+$ only decomposition was observed—initially proceeded much in the same manner as those of [(OC)$_5$W—C≡N—CHTos]$^-$. Corresponding triazoline complexes (**11a–15a**) were eluted from the column as yellow bands; however, each time these were followed by a deep red band which could be developed using a more polar solvent. Elemental analyses and molecular weights as taken from the mass spectra were identical for the two species, obviously isomers. In the red compounds **11b–15b**, a new IR absorption band was observed at about 2240 cm^{-1}, which was definitely too high for an isonitrile stretching vibration. Conductivity measurements also ruled out the possibility that this band was due to diazonium counterions in saltlike complexes. According to the ^{13}C NMR spectra, the red isomers contain no carbene carbon; however, there is a new resonance at ca. 120 ppm, i.e., in a range typical of *nitriles*. Since ^{183}W satellites are absent, this carbon atom is not directly bonded to the metal, suggesting an N-coordinated nitrile ligand. This is in accord with the above-mentioned IR feature as well as with the mass spectra of **11b–15b**, which unlike those of the carbene complexes **11a–15a** are dominated by the "ligand-free" ions [M(CO)$_n$]$^+$ (n = 6–0), as expected for weakly bonded nitrile complexes.

Both proposed products have been confirmed by X-ray structure analyses (see below).

We feel that the formation of both the carbene and the nitrile ligand can be rationalized by a single mechanism which in the first step offers two possibilities for [3 + 2] cycloadditions leading to the regioisomeric 5- (route A) and 3-metallo-1,2,4-triazoles (route B) (Scheme I). While the former are stable products (**11a–15a**), the heterocyclic betaines are assumed to suffer NN bond breakage, followed by a 1,2-shift of the metal from C^3 to N^2 and some tautomerization to give the conjugated cyanimide systems **11b–15b**. Note that along route B the NN triple bond of the diazonium group is successively cleaved while at the same time ethyl isocyanoacetate is formally inserted.

As has been shown by van Leusen et al., "free" TOSMIC and aryldiazonium salts also yield mixtures of regioisomeric 1,2,4-triazoles. By the way, these are the only *non*regiospecific [3 + 2] cycloadditions of α-metalated isocyanides described in the literature,[7] just as the reactions discussed in this paragraph are the first examples of *non*regiospecific 1,3-dipolar cycloadditions with metallo nitrile ylides.

NN bond cleavage adjacent to a metal–carbon bond followed by some arrangement to give metal–N-bonded products is a common reaction sequence in organometallic chemistry. In this way, using N-nucleophiles such as N$_3^-$

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Table I. Selected IR and Mass Spectroscopic Data for the Complexes 1–5 and 11a,b–15a,b

	IR (cm^{-1}, KBr)			MS [m/z (rel intens)]		
	ν(NH)	ν(CO)	ν(triazoline)	[M(CO)$_5$L]$^+$	[ML]$^+$	[L]$^+$
1	3269 m	2066 s, 1965 s, 1909 vs, 1888 sh	1496 m, 1429 m	623 (13)	483 (23)	299 (10)
2	3316 m	2070 s, 1970 sh, 1964 s, 1914 vs, 1886 vs	1490 m, 1422 m	657 (7)	517 (12)	333 (4)
3	3315 m	2069 m, 1965 m, 1912 vs, 1886 vs	1604 w, 1512 m, 1425 w	653 (8)	513 (4)	329 (100)
4[a]	3308 m	2069 m, 1965 m, 1912 vs, 1886 vs	1609 w, 1493 w, 1423 w	668 (1)	528 (5)	344 (14)
5	3325 m	2067 m, 1972 s, 1907 vs, 1872 vs	1608 w, 1433 w	666 (1)	526 (1)	342 (100)
11a	3294 s	2061 s, 1978 s, 1903 vs	1497 m, 1395 m, 1226 m	409 (7)	269 (4)	217 (12)
12a	3307 m	2062 s, 1971 s, 1899 vs	1494 m, 1399 m, 1226 m	443 (6)	303 (65)	251 (5)
13a	3299 s	2060 s, 1978 s, 1902 vs	1513 m, 1399 m, 1235 m	423 (20)	283 (100)	231 (5)
14a	3294 s	2066 s, 2001 s, 1903 vs	1498 m, 1400 s, 1228 m	541 (26)	401 (58)	217 (3)
15a	3307 m	2067 s, 1967 s, 1892 vs	1494 m, 1395 m, 1228 m	575 (24)	435 (51)	251 (3)

	IR (cm^{-1}, KBr)				MS [m/z (rel intens)]		
	ν(NH)	ν(N≡C)	ν(CO)	ν(N=C)	[M(CO)$_5$L]$^+$	[ML]$^+$	[L]$^+$
11b[b]	3340 m	2244 m	2069 w, 1950 s, 1908 vs, 1881 vs, 1858 sh	1636 s	[c]	[c]	[c]
12b[b]	3308 m	2245 m	2070 s, 2001 sh, 1995 s, 1927 vs, 1853 vs	1620 s	443 (18)[d]	303 (12)[d]	251 (15)[d]
13b[b]	3334 m	2247 m	2069 m, 1989 m, 1918 vs, 1866 vs	1626 s	390 (8)	[c]	231 (9)
14b[b]	3314 m	2241 m	2073 m, 1973 s, 1924 vs, 1846 vs	1631 s	541 (1)	401 (6)	217 (50)
15b[b]	3293 m	2241 m	2072 s, 2001 sh, 1988 s, 1917 vs, 1846 vs	1616 s	575 (3)	435 (12)	251 (35)

[a] 1524 m, 1344 m [ν(NO$_2$)]. [b] Also observed: M(CO)$_n^+$ (n = 6–0). [c] Not observed. [d] (–)-FAB in MNBA/glycerine.

or amines, carbene, carbyne, and N-isocyanide ligands have been converted to nitriles or cyanamides, respectively.[14,15] Similarly, isocyanato complexes are formed from metal carbonyls and nitrogen sources[16,17] or, conversely, from complex-bound azide and CO, presumably via the same transition state.[18] Even NN double bonds are mildly cleaved with the help of transition-metal complexes, a process of biological interest, as there is evidence that diimine is an intermediate in the enzymatic reduction of molecular nitrogen.[19]

Structure of 11a. The molecular structure of **11a** together with the atomic numbering scheme is shown in Figure 1. Bond distances and bond angles are given in Table III, while the atomic coordinates are listed in Table IV.

The central part of the molecule consists of a five-membered planar heterocycle with phenyl, carbethoxy, and pentacarbonylchromio substituents. The shortest bond in the ring is the C7–N2 double bond of 129.6(4) pm and the longest one the adjacent N2–N1 bond of 138.2(4) pm, which almost amounts to a single-bond length. (Very understandably, this will be the "target site of fracture" in the regioisomeric heterocycle (see Scheme I and below).) However, since the remaining CN bonds are absolutely equal in length, viz. 136.2 ± 0.3 pm, the bipartition of the triazole in **11a** into two localized π-systems—the C(N)N carbene and the opposite N=C(CO$_2$Et) function—is much less pronounced than that of the imidazolin-2-ylidene ligands in complex **16**[2f] and, particularly, in tetrakis(N-methylimidazolin-2-ylidene)palladium iodide (**17**).[20]

The Cr–C(carbene) bond length of 208.4(3) pm is remarkably short in comparison with the 211–213-pm distances frequently exhibited by this type of diaminocarbene complex.[21,22] Obviously, more than the usual back-donation from the metal to the electron-deficient carbene carbon is required to compensate for the relatively long C(carbene)–N bond distances.[23]

The bond angles about the heterocycle are as expected, with the slight asymmetry in the external angles at C6 serving the purpose of diminishing the repulsion between the carbonyl ligands and the phenyl ring. For the same reason, the phenyl ring is almost perpendicular to the heteroaromatic system, thus precluding any conjugative interaction.

With respect to the *cis*-CO ligands, the triazole ring plane takes up a staggered conformation; i.e., it approximately bisects the C1–Cr–C2 and C4–Cr–C5 angles (cf. Table XI, supplementary material).

In the crystal lattice, the molecules **11a** exist in pairs; the intermolecular linkage is effected by N—H···O hydrogen bridges (N···O = 295.8 pm) between the carboxyl oxygen atoms (O6) and the NH functions.

Structure of 12b. The molecular structure of **12b** is shown in Figure 2. The bond distances and angles are given in Table V; listings of the final positional and thermal parameters for the non-hydrogen atoms are given in Table VI.

The general impression is that of an extended ligand system which due to the accumulation of sp- and sp^2-hybridized C and N atoms is largely planar. This is borne out in more detail by the angle of less than 11° between the plane of the 4-chlorophenyl substituent (plane I) and the approximate plane of the central N-cyanamidine skeleton (plane III) and that between plane III and the carbethoxy function (plane II), which is just slightly over 14° (supplementary material, Table XII).

With angles of 175.1 and 168.9°, the atomic sequence Cr–N1–C6–N2 deviates considerably from linearity, an effect occasionally observed for the M–C–N–C chains in

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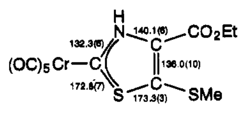
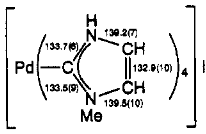
Table II. NMR Data for Complexes 1–5 and 11–15

	^{1}H NMR (δ)	^{13}C NMR (δ)
1^{a,e}	11.35 [1 H, s, NH], 8.1–7.6 [8 H, m Ar], 2.5 [3 H, s, $\mathrm{SO_2C_6H_4C}\mathit{H}_3$]	200.1, 196.7 [CO], 186.3 [C(carbene)], 153.7 [*C*Tos], 147.7, 132.3, 130.7, 129.3 [$\mathrm{SO_2}\mathit{C}_6\mathrm{H_4CH_3}$], 132.4, 129.8, 127.6, 127.5, [NAr], 21.9 [$\mathrm{SO_2C_6H_4}\mathit{C}\mathrm{H_3}$]
2^{b,d,f}	8.0–7.5 [8 H, m, Ar], 2.5 [3 H, s, $\mathrm{SO_2C_6H_4C}\mathit{H}_3$]	201.2, 197.0 [CO], 184.0 [C(carbene)], 148.3 [*C*Tos], 146.9, 134.1, 130.5, 129.7, [$\mathrm{SO_2}\mathit{C}_6\mathrm{H_4CH_3}$], 135.1, 130.0, 129.0, 128.5 [NAr], 21.2 [$\mathrm{SO_2C_6H_4}\mathit{C}\mathrm{H_3}$]
3^{a,e}	11.45 [1 H, s, NH], 8.05, 7.4 [2 × 2 H, 2 d, $\mathrm{SO_2C_6}\mathit{H}_4\mathrm{CH_3}$], 7.35, 6.95 [2 × 2 H, 2d, NAr], 3.85 [3 H, s, $\mathrm{OCH_3}$], 2.5 [3 H, s, $\mathrm{SO_2C_6H_4\text{-}C}\mathit{H}_3$]	200.3, 196.8 [CO], 186.6 [C(carbene)], 153.5 [*C*Tos], 147.6, 132.3, 130.7, 129.3 [$\mathrm{SO_2}\mathit{C}_6\mathrm{H_4CH_3}$], 161.3, 133.9, 128.9, 114.5 [NAr], 55.7 [$\mathrm{OCH_3}$], 21.9 [$\mathrm{SO_2C_6H_4}\mathit{C}\mathrm{H_3}$]
4^{b,d,f}	8.4–7.6 [8 H, m, Ar], 2.5 [3 H, s, $\mathrm{SO_2C_6H_4C}\mathit{H}_3$]	200.9, 196.9 [CO], 183.9 [C(carbene)], 148.0 [*C*Tos], 146.7, 134.0, 130.4, 129.6 [$\mathrm{SO_2}\mathit{C}_6\mathrm{H_4CH_3}$], 144.2, 129.6, 128.4, 124.2 [NAr], 21.1 [$\mathrm{SO_2C_6H_4}\mathit{C}\mathrm{H_3}$]
5^{b,d,g}	8.0, 7.6 [2 × 2 H, 2 d, $\mathrm{SO_2C_6}\mathit{H}_4\mathrm{CH_3}$], 7.3, 6.7 [2 × 2 H, 2 d, NAr], 2.95 [6 H, s, $\mathrm{NMe_2}$], 2.5 [3 H, s, $\mathrm{SO_2C_6H_4C}\mathit{H}_3$]	202.0, 198.0 [CO], 186.3 [C(carbene)], 152.9 [*C*Tos], 148.3, 136.3, 131.4, 129.7, 112.4 [Ar], 40.4 [$\mathrm{NMe_2}$], 21.7 [$\mathrm{SO_2C_6H_4}\mathit{C}\mathrm{H_3}$]
11a^{a,e}	10.85 [1 H, s, NH], 7.65–7.4 [5 H, m, Ar], 4.6 [2 H, q, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 1.4 [3 H, t, $\mathrm{OCH_2C}\mathit{H}_3$]	220.4, 216.4 [CO], 202.6 [C(carbene)], 156.3 [$\mathit{C}\mathrm{O_2Et}$], 144.8 [$\mathit{C}\mathrm{CO_2Et}$], 139.5, 130.7, 129.5, 127.7 [Ar], 63.9, 14.1 [OEt]
11b^{c,e}	10.9 [1 H, s, NH], 7.7–7.4 [5 H, m, Ar], 4.55 [2 H, q, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 1.4 [3 H, t, $\mathrm{OCH_2C}\mathit{H}_3$]	220.5, 214.4 [CO], 121.7 [N≡C], 156.8 [$\mathit{C}\mathrm{O_2Et}$], 152.0 [$\mathit{C}\mathrm{CO_2Et}$], 134.6, 129.7, 128.1 [Ar], 66.0, 14.0 [OEt]
12a^{a,e}	10.95 [1 H, s, NH], 7.45, 7.3 [2 × 2 H, 2 d, Ar], 4.5 [2 H, q, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 1.4 [3 H, t, $\mathrm{OCH_2C}\mathit{H}_3$]	220.2, 216.4 [CO], 203.3 [C(carbene)], 156.5 [$\mathit{C}\mathrm{O_2Et}$], 145.1 [$\mathit{C}\mathrm{CO_2Et}$], 137.9, 136.9, 129.7, 129.1 [Ar], 64.2, 14.0 [OEt]
12b^{c,f}	10.7 [1 H, s, NH], 7.8, 7.5 [2 × 2 H, 2 d, Ar], 4.55 [2 H, q, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 1.45 [3 H, t, $\mathrm{OCH_2C}\mathit{H}_3$]	220.3, 213.1 [CO], 124.3 [N≡C], 157.4 [$\mathit{C}\mathrm{O_2Et}$], 155.9 [$\mathit{C}\mathrm{CO_2Et}$], 135.1, 130.2, 128.7, 125.1 [Ar], 63.7, 13.6 [OEt]
13a^{a,e}	11.0 [1 H, s, NH], 7.3 [4 H, m, Ar], 4.6 [2 H, q, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 2.4 [3 H, s, Me], 1.4 [3 H, t, $\mathrm{OCH_2C}\mathit{H}_3$]	220.5, 216.5 [CO], 202.3 [C(carbene)], 156.5 [$\mathit{C}\mathrm{O_2Et}$], 144.7 [$\mathit{C}\mathrm{CO_2Et}$], 140.9, 137.0, 129.9, 127.5 [Ar], 63.9, 14.1 [OEt], 21.3 [Me]
13b^{a,e}	8.8 [1 H, s, NH], 7.5, 7.2 [2 × 2 H, 2 d, Ar], 4.55 [2 H, q, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 2.4 [3 H, s, Me], 1.5 [3 H, t, $\mathrm{OCH_2C}\mathit{H}_3$]	220.6, 214.6 [CO], 121.6 [N≡C], 156.8 [$\mathit{C}\mathrm{O_2Et}$], 151.3 [$\mathit{C}\mathrm{CO_2Et}$], 138.0, 132.2, 130.1, 119.1 [Ar], 65.8, 14.1 [OEt], 21.1 [Me]
14a^{a,e}	11.35 [1 H, s, NH], 7.6–7.4 [5 H, m, Ar], 4.6 [2 H, q, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 1.5 [3 H, t, $\mathrm{OCH_2C}\mathit{H}_3$]	200.3, 196.9 [CO], 185.84 [C(carbene)], 156.7 [$\mathit{C}\mathrm{O_2Et}$], 145.0 [$\mathit{C}\mathrm{CO_2Et}$], 139.6, 130.7, 129.4, 127.6 [Ar], 64.2, 14.0 [OEt]
14b^{a,e}	8.9 [1 H, s, NH], 7.7–7.35 [5 H, m, Ar], 4.65 [2 H, q, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 1.5 [3 H, t, $\mathrm{OCH_2C}\mathit{H}_3$]	201.5, 197.0 [CO], 121.7 [N≡C], 156.7 [$\mathit{C}\mathrm{O_2Et}$], 151.9 [$\mathit{C}\mathrm{CO_2Et}$], 134.7, 129.7, 128.0 [Ar], 66.2, 14.1 [OEt]
15a^{a,e}	11.2 [1 H, s, NH], 7.55, 7.45 [2 × 2 H, 2 d, Ar], 4.6 [2 H, q, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 1.5 [3 H, t, $\mathrm{OCH_2C}\mathit{H}_3$]	200.0, 196.8 [CO], 186.4 [C(carbene)], 156.4 [$\mathit{C}\mathrm{O_2Et}$], 145.2 [$\mathit{C}\mathrm{CO_2Et}$], 138.1, 137.0, 129.7, 128.9 [Ar], 64.2, 14.1 [OEt]
15b^{a,e}	8.9 [1 H, s, NH], 7.6, 7.4 [2 × 2 H, 2 d, Ar], 4.6 [2 H, q, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$], 1.55 [3 H, t, $\mathrm{OCH_2C}\mathit{H}_3$]	201.4, 197.0 [CO], 122.9 [N≡C], 156.5 [$\mathit{C}\mathrm{O_2Et}$], 152.0 [$\mathit{C}\mathrm{CO_2Et}$], 133.5, 133.3, 129.8 [Ar], 66.3, 14.1 [OEt]

[a] ^{1}H NMR in $\mathrm{CDCl_3}$. [b] ^{1}H NMR in DMSO-d_6. [c] ^{1}H NMR in acetone-d_6. [d] δ[NH] not observed. [e] ^{13}C NMR in $\mathrm{CDCl_3}$. [f] ^{13}C NMR in DMSO-d_6. [g] ^{13}C NMR in acetone-d_6.



16



17

functional isocyanide complexes.[24] At the (2–3)σ level, the N≡C bonds in **12b** (115.0(5) pm), pentacarbonyl(*o*-tolunitrile)chromium (113.9(9) pm[25]), and pentacarbonyl-(*N*,*N*-diethylcyanamide)chromium (18) (113.9(5) pm[26]) are equal in length, and so are the adjacent C–N bonds in **12b** (132.3(5) pm) and 18 (131.4(5) pm). Just as in the other two complexes, the Cr–N distance in **12b** is shorter than the sum of the covalent radii, perhaps reflecting some weak π-contribution to this bond. The strong σ-donor character of the nitrile ligand finds its expression in the severe shortening of the *trans* metal–C bond (Cr–C1 = 182.1(4) pm) as compared to the average Cr–CO_{cis} distance of 191.5 pm.

A question not completely answered by this structure determination concerns the position of the NH proton, which could be located either at N2 or at N3. However, the bond lengths to C7 and the angles about this carbon atom are definitely in favor of the cyan*imine* tautomer (cf. Scheme I and Table V).

Metal–Ligand Bond Cleavage. There are several methods of cleaving the carbene ligand off the metal, the ones most frequently used being thermolysis[27] or oxidative degradation of the complex, by which the carbene carbon is converted into a carbonyl group.[28]

The reaction of **15a** with a mixture of $\mathrm{KMnO_4/Fe(NO_3)_3}$ in acetone/water followed by centrifugation and extraction with diethyl ether now led to the colorless solid **19**. The spectroscopic data (Experimental Section) are perfectly

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(24) Cf., e.g.: Christian, G.; Stolzenberg, H.; Fehlhammer, W. P. *J. Chem. Soc., Chem. Commun.* **1982**, 184.

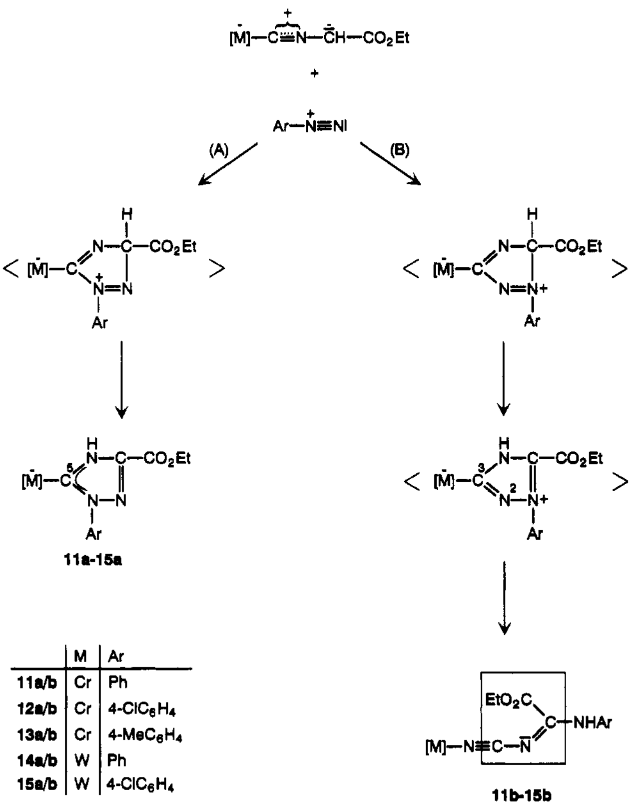
(25) Denise, B.; Massoud, A.; Parlier, A.; Rudler, H.; Daran, J. C.; Vaissermann, J.; Alvarez, C.; Patino, R.; Toscano, R. A. *J. Organomet. Chem.* **1990**, *386*, 51.

(26) Schubert, U.; Neugebauer, D.; Friedrich, P. *Acta Crystallogr.* **1978**, *B34*, 2293.

(27) E.g.: Fischer, E. O.; Dötz, K. H. *J. Organomet. Chem.* **1972**, *36*, C4.

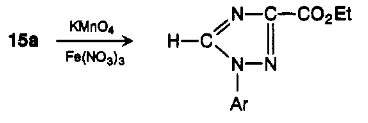
(28) Cf., e.g.: Aumann, R.; Kuckert, E. *Chem. Ber.* **1986**, *119*, 156. Aumann, R.; Heinen, H. *Chem. Ber.* **1987**, *120*, 1297.

Scheme I



	M	Ar
11a/b	Cr	Ph
12a/b	Cr	4-ClC$_6$H$_4$
13a/b	Cr	4-MeC$_6$H$_4$
14a/b	W	Ph
15a/b	W	4-ClC$_6$H$_4$

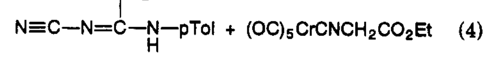
in accord with the proposed structure (eq 3); i.e., oxidation affects only the metal fragment, which subsequently releases the tautomerized 1-phenyl-3-carbethoxy-1,2,4-triazole.



(3)

19

The lability of the nitrile ligand in complexes, particularly in those of low-valent metals, is common knowledge. To remove the *N*-cyanamidine ligand from complex **13b**, ethyl isocyanoacetate was added to its solution in dichloromethane. After 3 days at room temperature, the red color of the solution had disappeared and a colorless solid with a strong IR absorption at 2193 cm^{-1} (ν(C≡N)) was isolated together with the starting complex Cr(CO)$_5$-CNCH$_2$CO$_2$Et (eq 4).



$$\mathbf{13b} + \mathrm{CNCH_2CO_2Et} \longrightarrow \mathrm{N{\equiv}C{-}N{=}}\overset{\mathrm{CO_2Et}}{\mathrm{C}}\mathrm{{-}}\underset{\mathrm{H}}{\mathrm{N}}\mathrm{{-}pTol} + \mathrm{(OC)_5CrCNCH_2CO_2Et} \quad (4)$$

20

Compounds of the type N≡C—NH—CR=NR′ and N≡C—N=CR—NHR′ are interesting synthons on the way to biologically important compounds.[29] A purely organic route to *N*-cyanamidines consists of the reaction of methyl 3,3-diazido-2-cyanoacrylate with anilines, which proceeds with elimination of two molecules of nitrogen and one molecule of HCN.[30]

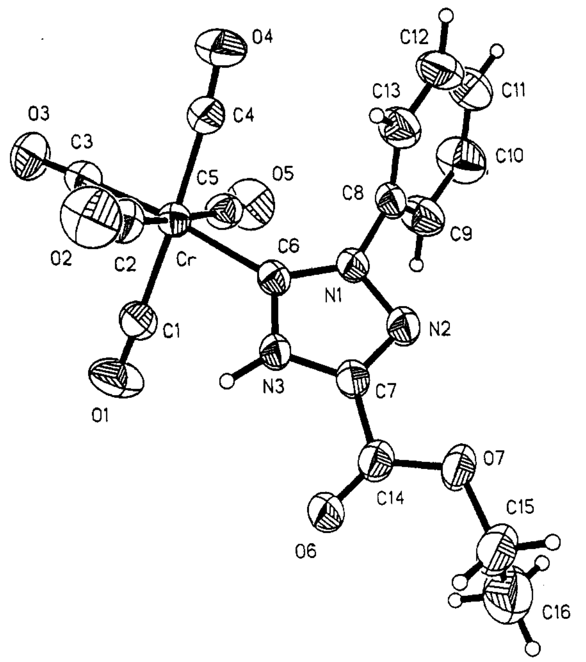


Figure 1. Molecular structure of **11a**. The thermal ellipsoids are drawn at the 50% probability level.

Table III. Important Bond Lengths (pm) and Angles (deg) for Compound 11a[a]

	Bond Lengths		
Cr–C1	190.7(3)	Cr–C2	188.6(3)
Cr–C3	187.4(4)	Cr–C4	188.3(3)
Cr–C5	190.7(3)	Cr–C6	208.4(3)
O7–C14	131.9(4)	O6–C14	119.4(4)
N1–N2	138.2(4)	N1–C6	136.2(4)
N1–C8	143.9(4)	N2–C7	129.6(4)
N3–C6	136.5(4)	N3–C7	136.0(4)
C7–C14	148.7(5)		
	Bond Angles		
N2–N1–C6	114.5(2)	N2–N1–C8	116.1(2)
C6–N1–C8	129.3(3)	N1–N2–C7	103.1(2)
C6–N3–C7	110.7(2)	Cr–C6–N1	132.8(2)
N1–C6–N3	100.6(3)	Cr–C6–N3	126.2(2)
N2–C7–C14	125.0(3)	N2–C7–N3	111.0(3)
N3–C7–C14	124.0(3)	O6–C14-O7	126.9(3)
O7–C14–C7	109.9(3)	O6–C14–C7	123.1(3)

[a] Standard deviations in parentheses; see Figure 1 for atomic numbering.

Experimental Section

All operations were carried out under an inert-gas atmosphere (Ar) using Schlenk tube techniques. All solvents were deoxygenated with the organic solvents dried prior to use. IR spectra were recorded on a Perkin Elmer 983 spectrometer. C, H, and N analyses were obtained with a Heraeus CHN-Rapid-Elementaranalysator. Melting points were taken on a Gallenkamp melting point apparatus and are uncorrected. FAB mass spectra were obtained with a CH5-DF Varian MAT device (Bremen) and EI mass spectra (80 eV) with a Varian MAT 711 (Bremen) instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AM 250 and 270 instruments; the solvent was used as an internal standard. Conductivity measurements were carried out on a Metrohm E 518 Conductometer. Silica gel (100-200 μm)

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(29) Ishimitsu, K.; Suzuki, J.; Ohishi, H.; Yamada, T.; Hatano, R.; Takakusa, N.; Mitsui, J. PCT Int. Appl. WO 91 04,965; *Chem. Abstr.* **1991**, *115*, 92085a. Ohtuka, K.; Ishiyama, N.; Iida, Y.; Seri, K.; Murai, T.; Sanai, K.; Ishizaka, Y. Eur. Pat. Appl. EP 412,531; *Chem. Abstr.* **1991**, *115*, 49406u. Shiokawa, Y.; Takimoto, K.; Takenaka, K.; Kato, T. Eur. Pat. Appl. EP 389,861; *Chem. Abstr.* **1991**, *114*, 164007f.

(30) Saalfrank, R. W.; Ackermann, E.; Fischer, M.; Wirth, U.; Zimmermann, H. *Chem. Ber.* **1990**, *123*, 115. Saalfrank, R. W.; Lurz, C. J.; Hassa, J.; Danion, D.; Toupet, L. *Chem. Ber.* **1991**, *124*, 595.

Table IV. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($pm^2 \times 10^{-1}$) for Complex 11a[a]

atom	*x/a*	*y/b*	*z/c*	U^b
Cr	1768(1)	691(1)	7012(1)	37(1)
O1	6076(4)	−990(2)	7047(2)	75(1)
O2	−827(4)	−579(2)	8871(2)	85(1)
O3	1031(4)	−1118(2)	5626(2)	76(1)
O4	−2542(4)	2202(2)	6760(2)	73(1)
O5	3905(4)	2132(2)	5109(2)	73(1)
O6	5830(4)	1251(2)	10470(2)	53(1)
O7	5279(4)	3339(2)	10351(2)	69(1)
N1	2506(4)	3053(2)	7982(2)	37(1)
N2	3439(4)	3411(2)	8718(2)	43(1)
N3	3524(4)	1402(2)	8812(2)	36(1)
C1	4466(6)	−360(3)	7052(2)	45(1)
C2	216(6)	−117(3)	8180(3)	50(2)
C3	1288(5)	−423(3)	6147(3)	48(1)
C4	−895(5)	1669(3)	6872(3)	45(1)
C5	3141(5)	1602(3)	5831(3)	45(1)
C6	2554(5)	1807(2)	7997(2)	34(1)
C7	4030(5)	2370(3)	9212(2)	40(1)
C8	1683(5)	4032(3)	7297(2)	38(1)
C9	3123(6)	4611(3)	6585(3)	58(2)
C10	2354(7)	5613(3)	5972(3)	73(2)
C11	175(7)	6008(3)	6083(3)	74(2)
C12	−1236(7)	5423(3)	6791(3)	72(2)
C13	−493(6)	4430(3)	7423(3)	55(2)
C14	5160(5)	2234(3)	10086(2)	44(1)
C15	6498(7)	3402(3)	11150(3)	67(2)
C16	8717(7)	3494(3)	10634(3)	90(2)

[a] Standard deviations in parentheses. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

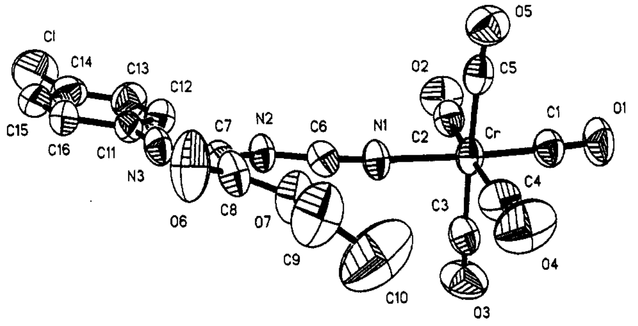

Figure 2. Molecular structure and labeling scheme of complex **12b**. The thermal ellipsoids are drawn at the 50% probability level.

Table V. Important Interatomic Distances (pm) and Bond Angles (deg) for Complex 12b[a]

	Bond Distances		
Cr–N1	207.1(3)	Cr–C1	182.1(4)
Cr–C2	189.7(4)	Cr–C3	192.5(5)
Cr–C4	191.2(4)	Cr–C5	192.6(5)
N1–C6	115.0(5)	N2–C6	132.3 (5)
N2–C7	129.7(4)	N3–C7	133.6(5)
N3–C11	141.2(5)	O6–C8	119.0(5)
O7–C8	129.7(5)	C7–C8	152.4(5)
	Bond Angles		
Cr–N1–C6	175.1(3)	N1–C6–N2	168.9(4)
C6–N2–C7	125.1(3)	C7–N3–C11	130.4(3)
N2–C7–N3	122.4(3)	N2–C7–C8	126.6(3)
N3–C7–C8	111.0(3)	O7–C8–C7	111.7(3)
O6–C8–O7	127.5(4)	O6–C8–C7	120.8(4)

[a] Estimated standard deviations are given in parentheses.

Table VI. Fractional Coordinates ($\times 10^4$) and Thermal Parameters ($pm^2 \times 10^{-1}$) for 12b[a]

	x/a	*y/b*	*z/c*	U^b
Cr	1012(1)	9434(1)	7115(1)	49(1)
Cl	−1086(2)	16437(1)	1384(1)	116(1)
N1	−468(4)	11079(3)	6819(2)	53(1)
N2	−1784(4)	12989(2)	6115(2)	50(1)
N3	−3241(4)	14929(2)	6142(3)	50(1)
O1	3425(5)	7112(2)	7425(3)	86(2)
O2	3657(4)	9212(3)	4705(2)	84(2)
O3	−1976(5)	8275(3)	6465(3)	101(2)
O4	−1300(6)	9244(4)	9655(3)	124(2)
O5	4097(5)	10416(3)	7868(3)	78(1)
O6	−4244(5)	14986(3)	8359(2)	104(2)
O7	−3522(4)	13057(2)	8444(2)	71(1)
C1	2461(6)	8009(3)	7309(3)	58(2)
C2	2614(6)	9347(3)	5596(3)	55(2)
C3	−904(6)	8736(3)	6700(3)	62(2)
C4	−522(7)	9377(4)	8654(4)	71(2)
C5	2926(6)	10093(3)	7577(3)	53(2)
C6	−1181(5)	11993(3)	6585(3)	48(2)
C7	−2801(5)	13924(3)	6662(3)	47(2)
C8	−3608(6)	14054(4)	7938(3)	60(2)
C9	−4194(8)	13090(5)	9684(4)	105(3)
C10	−4501(11)	12028(6)	10109(5)	168(5)
C11	−2674(5)	15228(3)	4989(3)	49(2)
C12	−1523(6)	14457(3)	4134(3)	58(2)
C13	−1045(6)	14826(4)	3025(4)	69(2)
C14	−1706(6)	15967(4)	2770(4)	70(2)
C15	−2872(6)	16745(4)	3615(4)	74(2)
C16	−3338(5)	16375(3)	4714(4)	62(2)

[a] Estimated standard deviations are given in parentheses. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

from ICN was used for column chromatography. The aryldiazonium salts $[ArN_2]BF_4$ (Ar = Ph, 4-ClC_6H_4, 2,4,6-$Me_3C_6H_2$, 4-MeC_6H_4, 4-$O_2NC_6H_4$, 4-$Me_2NC_6H_4$, 4-$MeOC_6H_4$),[31] $CNCH_2CO_2Et$,[32] $Cr(CO)_5CNCH_2CO_2Et$,[2f] $W(CO)_5CNCH_2CO_2Et$,[2f] $W(CO)_5$TOSMIC,[2c] and $[Pt(Cl)(CNCH_2CO_2Et)(PPh_3)_2]BF_4$[33] were prepared by published methods. All other reagents were purchased from Aldrich. Analytical data and physical properties of the new complexes are given in Table VII.

1. (1-Aryl-3-tosyl-1,2,4-triazolin-5-ylidene)pentacarbonyltungsten (1–5): General Procedure. To a stirred solution of 0.52 g (1.0 mmol) of $W(CO)_5$TOSMIC in 10 mL of THF was added 0.7 mL of $LiBu^n$ (15% solution in *n*-hexane) in one portion at −78 °C (ethanol/dry ice). After 10 min, this was followed by the addition of 1.0 mmol of the solid aryldiazonium salt. This mixture, which changed color to red, was stirred for several hours at low temperature and then warmed to room temperature overnight. The solvent was evaporated in vacuo and the red, oily residue dissolved in CH_2Cl_2. After filtration, silica gel was added and the mixture evaporated to dryness. The resulting powder was transferred to a chromatography column charged with silica gel (2 × 25 cm) and eluted with *n*-hexane/diethyl ether (1/1) which gradually was changed into a 2/3 mixture; the pale yellow to yellow products were analytically pure right away.

For spectroscopic data, see Tables I and II; for elemental analyses and physical properties, see Table VII.

2. (1-Aryl-3-carbethoxy-1,2,4-triazol-5-ato)chlorobis(triphenylphosphine)platinum(II) (6–8): General Procedure. A 0.48-g (0.5-mmol) amount of $[Pt(Cl)(CNCH_2CO_2Et)(PPh_3)_2]BF_4$ was dissolved in 10 mL of CH_2Cl_2 and cooled with an ice bath. To this solution, first 0.14 mL (1.0 mmol) of NEt_3 and then 0.5 mmol of the aryldiazonium salt were added with stirring. After 3 h of stirring the resulting red solution was slowly warmed to room temperature and evaporated to dryness. In order to remove NEt_3HBF_4, the residue was extracted with acetone, in which the platinum complex is insoluble. The solid was collected on a frit, washed with acetone, and recrystallized several times from dichloromethane/*n*-hexane to give a colorless pure product.

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(31) Tröndlin, F.; Rüchardt, C. *Chem. Ber.* **1977**, *110*, 2504. Aryldiazonium salts not described therein were prepared analogously.

(32) Hartman, G. D.; Weinstock, L. M. *Org. Synth.* **1980**, *59*, 183. In contrast to the procedure given here, the temperature should be kept at 5 °C and *not* at 25–30 °C in step B while adding Na_2CO_3.

(33) Fehlhammer, W. P.; Herrmann, W. A.; Öfele, K. In *Handbuch der Präparativen Anorganischen Chemie*; Brauer, G., Ed.; Enke Verlag: Stuttgart, Germany, 1981; Vol. III, p 2015f.

Table VII. Analytical and Other Data

compd no.	formula (mol wt)	anal. calcd (found) (%) C	H	N	mp (°C)	yield (%)
1	$C_{20}H_{13}N_3O_7SW$ (623.25)	38.54 (38.64)	2.10 (2.30)	6.74 (6.94)	181 dec	73
2	$C_{20}H_{12}ClN_3O_7SW$ (657.70)	36.52 (36.61)	1.84 (2.01)	6.39 (6.14)	152 dec	59
3	$C_{21}H_{15}N_3O_8SW$ (653.28)	38.61 (38.96)	2.31 (2.59)	6.43 (6.22)	157 dec	42
4	$C_{20}H_{12}N_4O_9SW$ (668.25)	35.94 (35.36)	1.81 (1.91)	8.38 (8.17)	189 dec	53
5	$C_{22}H_{18}N_4O_7SW$ (666.33)	39.66 (39.32)	2.72 (2.83)	8.41 (8.41)	198 dec	44
6	$C_{47}H_{40}ClN_3O_2P_2Pt$ (971.33)	58.08 (57.56)	4.15 (4.23)	4.33 (4.08)	268 dec	35
7	$C_{50}H_{46}ClN_3O_2P_2Pt$ (1013.42)	59.26 (58.61)	4.58 (4.55)	4.15 (4.19)	272 dec	59
8	$C_{47}H_{39}Cl_2N_3O_2P_2Pt$ (1005.78)	56.13 (56.03)	3.91 (4.18)	4.18 (4.25)	254 dec	42
9	$C_{47}H_{41}BClF_4N_3O_2P_2Pt$ (1059.16)	53.30 (52.44)	3.90 (4.01)	3.97 (3.74)	162	45
10	$C_{50}H_{47}BClF_4N_3O_2P_2Pt$ (1100.90)	54.53 (54.28)	4.30 (4.11)	3.82 (4.15)	170	47
11a	$C_{16}H_{11}CrN_3O_7$ (409.28)	46.94 (47.04)	2.71 (2.90)	10.27 (9.90)	149 dec	38
11b	$C_{16}H_{11}CrN_3O_7$ (409.28)	46.94 (46.64)	2.71 (2.98)	10.27 (10.09)	103 dec	23
12a	$C_{16}H_{10}ClCrN_3O_7$ (443.72)	43.31 (42.63)	2.27 (2.40)	9.47 (9.41)	143 dec	44
12b	$C_{16}H_{10}ClCrN_3O_7$ (443.72)	43.31 (42.61)	2.27 (2.50)	9.47 (9.47)	98 dec	30
13a	$C_{17}H_{13}CrN_3O_7$ (423.30)	48.24 (47.92)	3.10 (3.39)	9.93 (9.64)	142 dec	40
13b	$C_{17}H_{13}CrN_3O_7$ (423.30)	48.24 (47.93)	3.10 (3.25)	9.93 (9.82)	122 dec	28
14a	$C_{16}H_{11}N_3O_7W$ (541.13)	35.51 (35.75)	2.05 (2.12)	7.76 (7.72)	164 dec	42
14b	$C_{16}H_{11}N_3O_7W$ (541.13)	35.51 (35.55)	2.05 (2.06)	7.76 (7.57)	133 dec	28
15a	$C_{16}H_{10}ClN_3O_7W$ (575.58)	33.39 (33.33)	1.75 (1.78)	7.30 (7.23)	160 dec	40
15b	$C_{16}H_{10}ClN_3O_7W$ (586.12)	33.39 (32.95)	1.75 (1.86)	7.30 (7.27)	125 dec	24
19	$C_{11}H_{10}ClN_3O_2$ (251.67)	52.49 (52.44)	4.00 (3.82)	16.69 (15.99)	121	50
20	$C_{12}H_{13}N_3O_2$ (231.25)	62.33 (62.71)	5.67 (5.68)	18.17 (17.94)	83	95

Table VIII. Crystallographic Data

	11a	**12b**
formula	$C_{16}H_{11}N_3O_7Cr$	$C_{16}H_{10}N_3O_7CrCl$
mol wt	409.3	443.7
cryst color, habit	yellow needles	red plates
cryst size (mm)	0.64 × 0.1 × 0.08	0.26 × 0.46 × 0.09
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
unit cell dimens		
a (pm)	645.68(8)	710.2(2)
b(pm)	1098.66(13)	1180.4(4)
c(pm)	1329.83(15)	1236.2(3)
α (deg)	84.112(9)	86.49(3)
β (deg)	76.929(10)	73.62(2)
γ (deg)	79.054(10)	78.02(3)
V (10^6 pm^3)	900.4(2)	972.6(5)
Z	2	2
F(000)	416	448
density, calcd (Mg·m^{-3})	1.510	1.515
abs coeff, Mo Kα (mm^{-1})	0.660	0.752
temp (K)	295	295
total no. of measd rflns	3576	4642
no. of unique data	3198	4254
R_{int}	0.0055	0.0206
$\lvert F\rvert > 3\sigma_{\lvert F\rvert}$	2508	3098
no. of refined params	249	256
residuals		
R	0.0507	0.0608
R_w	0.0333	0.0426
R_g	0.0211	0.0299
weighting scheme w	$\sigma^{-2}_{\lvert F\rvert}$	$\sigma^{-2}_{\lvert F\rvert}$
largest features in final diff Fourier synthesis (10^6 e·pm^{-3})	+0.47/−0.37	+0.58/−0.53

IR (KBr, cm^{-1}): **6**, 1479 s, 1433 s, 1397 m ν(triazole ring), 300 w ν(PtCl); **7**, 1479 w, 1433 m, 1413 w ν(triazole ring), 304 w ν(PtCl); **8**, 1480 m, 1433 s, 1395 w ν(triazole ring), 306 w ν(PtCl). MS (EI): *m/z* **6**, 971 (M$^+$, 5%), **7**, 1013 (M$^+$, 1%), **8**, 1005 (M$^+$, 1%). ^{1}H NMR (δ, $CDCl_3$): **6**, 7.6–7.0 [35 H, m, PPh_3 + NAr], 4.3 [2 H, q, OCH_2CH_3], 1.3 [3 H, t, OCH_2CH_3]; **7**, 7.55–7.2 [30 H, m, PPh_3], 6.8 [2 H, s, NAr], 4.35 [2 H, q, OCH_2CH_3], 2.35 [3 H, s, *p*-Me], 1.45 [6 H, s, *o*-Me], 1.3 [3 H, t, OCH_2CH_3]. ^{13}C NMR (δ, $CDCl_3$): **6**, 160.5 [PtC], 156.1 [CO_2Et], 139.4, 134.5 vt ($J_{AX+AX'}$ = 5.77 Hz), 130.5, 130.1, 129.4 (AXX′, $J_{AX+AX'}$ = 29.06 Hz), 128.8, 128.1 vt ($J_{AX+AX'}$ = 5.28 Hz), 127.2, 124.0 [Ar + (CCO_2Et)], 60.1, 14.5 [OEt]; **7**, 160.7 [PtC], 154.9 [CO_2Et], 137.9, 136.5, 136.3, 134.9 vt ($J_{AX+AX'}$ = 5.94 Hz), 130.4, 130.3, 129.5 (AXX′, $J_{AX+AX'}$ = 29.34 Hz), 127.9 vt ($J_{AX+AX'}$ = 5.28 Hz) [Ar + $C(CO_2$Et)], 60.7, 14.5 [OEt], 21.0, 20.0 [Me]. For physical properties, see Table VII.

3. (1-Aryl-3-carbethoxy-1,2,4-triazolin-5-ylidene)chlorobis(triphenylphosphine)platinum(II) Tetrafluoroborate (Aryl = Ph (9), 2,4,6-Me$_3$C$_6$H$_2$ (10)). A 195-mg (0.2-mmol) amount of **6** [0.20 g (0.2 mmol) of **7**] was dissolved in 5 mL of CH_2Cl_2. To this solution was added 3 drops of ethereal HBF_4, and after 5 min of vigorous stirring the solvent was removed *in vacuo*. The residue was stirred with diethyl ether, and the colorless solid that resulted was dried *in vacuo*.

IR (KBr, cm^{-1}): **9**, 3229 m, b ν(NH), 1480 w, 1433 m, 1403 w ν(triazole ring), 321 w ν(PtCl); **10**, 3224 m, b ν(NH), 1479 w, 1433 m, 1406 w ν(triazole ring), 321 w ν(PtCl). ^{1}H NMR (δ, DMSO-d_6): **9**, 14.55 [1 H, s, NH], 7.85–7.3 [35 H, m, PPh_3 + NAr], 4.35 [2 H, q, OCH_2CH_3], 1.3 [3 H, t, OCH_2CH_3]; (δ, $CDCl_3$) **10**, 14.5 [1 H, s, NH], 7.65–7.3 [30 H, m, PPh_3], 6.8 [2 H, s, NAr], 4.35 [2 H, q, OCH_2CH_3], 2.35 [3 H, s, *p*-Me], 1.5 [6 H, s, *o*-Me], 1.35 [3 H, t, OCH_2CH_3]. ^{13}C NMR (δ, DMSO-d_6): **9**, 145.7 [C(carbene)], 154.5 [CO_2Et], 136.7, 133.8 vt ($J_{AX+AX'}$ = 5.67 Hz), 131.6 (AXX′, $J_{AX+AX'}$ = 28.96 Hz), 129.3, 128.8 vt ($J_{AX+AX'}$ = 5.27 Hz), 127.7, 127.3, 126.8, 122.3 [Ar + (CCO_2Et)], 63.1, 13.9 [OEt]. For physical properties, see Table VII.

4. (1-Aryl-3-carbethoxy-1,2,4-triazolin-5-ylidene)pentacarbonylchromium (11a–13a) and -tungsten (14a, 15a) and (*N*^{2}-Cyano-*N*^{1}-aryloxalamidine ethyl ester)pentacarbonylchromium (11b–13b) and -tungsten (14b, 15b): General Procedure. A 1.0-mmol amount of $M(CO)_5CNCH_2CO_2Et$ (M = Cr, W) was dissolved in 15 mL of THF and cooled to −78 °C (ethanol/dry ice). To this solution was added 0.7 mL of LiBu^n (15% in *n*-hexane) in one portion. After 5 min 1.0 mmol of solid aryldiazonium salt was added. The mixture was stirred for several hours at low temperature and then warmed to room temperature overnight. The solvent was evaporated and the red, oily residue extracted with dichloromethane. Silica gel was added to the extract, the solvent removed, and the residue placed on a silica gel column (2 × 25 cm) made up in *n*-hexane/diethyl ether (1/1). With a 1/1 mixture of *n*-hexane/diethyl ether a yellow band containing the triazolinylidene complex was eluted. Subsequent elution with *n*-hexane/diethyl ether (1/2) developed a red band from which the *N*-cyanamidine complex was isolated. Recrystallization from CH_2Cl_2/*n*-hexane afforded pure compounds. For spectroscopic data, see Tables I and II; for physical properties, see Table VII.

5. 1-(4-Chlorophenyl)-3-carbethoxy-1,2,4-triazole (19). A solution of 0.23 g (0.4 mmol) of **15a** in 15 mL of acetone was combined with a solution of 0.65 g (4.0 mmol) of $KMnO_4$ in 3 mL of water. A 200-mg (0.8-mmol) amount of $Fe(NO_3)_3·6H_2O$ was added in small portions with stirring. A heavy gas evolution was observed. The reaction mixture was stirred for another 1 h, repeatedly centrifuged, and finally filtered. The filtrate was carefully taken to dryness and the residue extracted with diethyl ether. After removal of the solvent, **19** remained as a white solid. Further purification is possible by silica gel chromatography with a 1/1 mixture of *n*-hexane/diethyl ether as eluent.

IR (KBr, cm^{-1}): 3129 m ν(CH), 1724 s $\nu(CO_2)$, 1486 m, 1450 m, 1230 m ν(triazole ring). MS (EI): *m/z* 251 (M$^+$, 79%), 206 ($[M - CO_2]^+$, 80%), 179 ($[M - CO_2Et]^+$, 100%). ^{1}H NMR (δ, $CDCl_3$): 4.5 [2 H, q, OCH_2CH_3], 2.45 [3 H, t, OCH_2CH_3], 7.5 [2 H, d, Ar], 7.7 [2 H, d, Ar], 8.65 [1 H, s, HC^5]. ^{13}C NMR (δ, $CDCl_3$): 159.5 [C^5], 156.0 [CO_2], 142.1 [CCO_2Et], 135.0, 130.7, 121.7 [Ar], 62.2, 14.2 [OEt]. For physical properties, see Table VII.

6. N^2-Cyano-N^1-(4-tolyl)oxalamidine Ethyl Ester (20). A 106-mg (0.25-mmol) amount of **13b** was dissolved in 3 mL of CH_2Cl_2. To this solution was added 0.03 mL (0.27 mmol) of ethyl isocyanoacetate in one portion. The mixture was stirred for 3 days at room temperature, during which time the color of the solution changed from red to yellow. Addition of 5 mL of *n*-hexane precipitated the organic product **20** as a white solid, which was collected, washed with 3/1 *n*-hexane/diethyl ether, and recrystallized from CH_2Cl_2/diethyl ether. The filtrate was evaporated to dryness, and the resulting yellow, viscous oil of $Cr(CO)_5CNCH_2CO_2Et$ was purified by Kugelrohr distillation.

IR (KBr, cm^{-1}): 3218 m, 3174 m ν(NH), 2193 s $\nu(N{\equiv}C)$, 1740 s $\nu_{as}(CO_2Et)$, 1614 s, 1597 s $\nu(N{=}C)$. IR (CH_2Cl_2, cm^{-1}): 3397 m, 3357 m ν(NH), 2190 s $\nu(N{\equiv}C)$, 1733 s $\nu_{as}(CO_2Et)$, 1632 m, 1607 m $\nu(N{=}C)$. MS (EI): *m/z* 231 (M$^+$, 44%), 158 ($[M - CO_2Et]^+$, 100%), 118 ($[4\text{-}CH_3C_6H_4NHC]^+$, 25%), 91 ($[4\text{-}CH_3C_6H_4]^+$, 43). ^{1}H NMR ($\delta$, $CDCl_3$): 8.6 [1 H, s, NH], 7.55 [2 H, d, Ar], 7.25 [2 H, d, Ar], 2.35 [3 H, s, Me], 4.55 [2 H, q, OCH_2CH_3], 1.4 [3 H, t, OCH_2CH_3]. For physical properties, see Table VII.

7. X-ray Crystal Structure Determinations. Single crystals of **11a** were grown by layering a concentrated acetone solution with *n*-hexane at −25 °C and those of **12b** in the same manner from a saturated CH_2Cl_2 solution. A preliminary peak search indicated the crystal system, and the space group was chosen. X-ray diffraction intensities were collected on a Siemens R3m/V four-circle diffractometer in the ω–2θ scan mode covering a half-sphere of reciprocal space up to $2\theta_{max} = 50°$ (**11a**) and $2\theta_{max} = 54°$ (**12b**), respectively. Numerical absorption and empirical extinction corrections have been applied. The phase problem was solved by direct methods employing the SHELXTL-Plus program package. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms have been placed into calculated positions and were included in the final cycles of refinement with isotropic displacement parameters. Further crystallographic data are compiled in Table VIII.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BMBW (Graduiertenkolleg *Syntheses and Structures of Low Molecular Compounds*).

Supplementary Material Available: Tables IX–XII, giving bonding parameters, best planes, and anisotropic thermal parameters for the non-hydrogen atoms of compounds **11a** and **12b** (6 pages). Ordering information is given on any current masthead page.

OM930198E