Journal of Organometallic Chemistry, 160 (1978) 101—108

OXIDATION OF ARENETRICARBONYLCHROMIUMS WITH NITROSYL CHLORIDE: A ROUTE TO NITROSYLCHROMIUM COMPLEXES *

MAX HERBERHOLD * and LUDWIG HAUMAIER

Anorganisch-chemisches Institut der Technischen Universität, Lothstr. 17, 8000 München 2 (B.R.D.)

(Received May 26th, 1978)

Summary

Polymeric dichlorodinitrosylchromium, $[CrCl_2(NO)_2]_n$, can be prepared by photonitrosylation of $Cr(CO)_6$ in CCl_4 solution or, preferably, by treating benzenetricarbonylchromium, $C_6H_6Cr(CO)_3$, with nitrosyl chloride in CH_2Cl_2 solution. The oxidative nitrosylation of arenetricarbonylchromiums, $ArCr(CO)_3$ (Ar = benzene or substituted benzene), with ClNO has been investigated in both THF and CH_2Cl_2 solution. Solvent-stabilised mononitrosylchromium intermediates of the type $[CrCl(CO)_2(NO)]$ are formed at low temperatures and converted into dinitrosylchromium complexes $[CrCl_2(NO_2]$ by further reaction with ClNO. Synthetic applications of these reactions are described.

Introduction

Chromium is the only metal for which a well-defined binary nitrosyl, $Cr(NO)_4$ [1,2], is known **. However, the chemistry of nitrosylchromium complexes appears to be far less well developed than that of nitrosyl-molybdenum and -tungsten compounds; in particular, only a limited number of halogenonitrosylchromium complexes has been reported (see reviews on nitrosylmetal complexes [4]).

The neglect of chromium is certainly due to the lack of general access to halogenonitrosylchromium compounds. In the case of molybdenum and tungsten, polymeric dichlorodinitrosyl complexes, $[MCl_2(NO)_2]_n$ (M = Mo [5], W [5,6]), are obtained by the reaction of the hexacarbonyls with nitrosyl chlo-

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[*] Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

[**] Other binary nitrosylmetal complexes have been reported, e.g. $Co(NO)_3$ [3a] and $Fe(NO)_4$ [3b]. However, there are still questions concerning the nature of these compounds. Thus, both $Co(NO)_3$ and $Fe(NO)_4$ are described as nonvolatile, in contrast to the highly volatile $Cr(NO)_4$.

ride at room temperature.

$$n\ M(CO)_6 + 2n\ ClNO \xrightarrow{CH_2Cl_2} [MCl_2(NO)_2]_n + 6n\ CO$$

(M = Mo, W)

$Cr(CO)_6$ does not react under these conditions.

A similar oxidative decarbonylation of "$MCl_2(CO)_4$" (M = Mo, W) with ClNO leads to the trichloromononitrosyl complex, $[MCl_3(NO)]_n$ [7], contaminated with the dinitrosyl, $[MCl_2(NO)_2]_n$. On the other hand, the reaction of $MoCl_2(CO)_4$ with nitric oxide gives $[MoCl_2(NO)_2]_n$ directly [8]. The corresponding "$CrCl_2(CO)_4$" is unknown.

The chloronitrosylmetal complexes of molybdenum and tungsten are also accessible by reductive nitrosylation of $MoCl_5$ [9—12,14] and WCl_6 [9,12—14] in solution; nitric oxide thereby functions as both the reducing agent and the incoming ligand. These studies appear not to have been extended successfully to $CrCl_3$. The direct reaction of $CrCl_2$ with NO in the presence of donor solvents has been described [6,15], but the reaction generally stops at the $[Cr(NO)L_5]Cl_2$ stage (L = H_2O, MeOH, EtOH, NH_3 [15]).

To prepare the unknown dichlorodinitrosylchromium, $[CrCl_2(NO)_2]_n$, from the kinetically inert $Cr(CO)_6$ (I), we considered two possibilities: (a) photoelimination of a CO ligand, i.e. photonitrosylation of I in CCl_4 solution; (b) use of a more reactive derivative of I, e.g. benzenetricarbonylchromium, $C_6H_6Cr(CO)_3$ (II), for reaction with ClNO in CH_2Cl_2 solution.

Both methods lead to the desired $[CrCl_2(NO)_2]_n$ (III) which is polymeric in non-coordinating solvents. The second route is preferable. The course of the reaction between arenetricarbonylchromiums, $ArCr(CO)_3$ (Ar = benzene (II) or substituted benzene), and nitrosyl chloride has been studied in both tetrahydrofuran and dichloromethane solution.

A. Preparation of $[CrCl_2(NO)_2]_n$ (III) (Scheme 1)

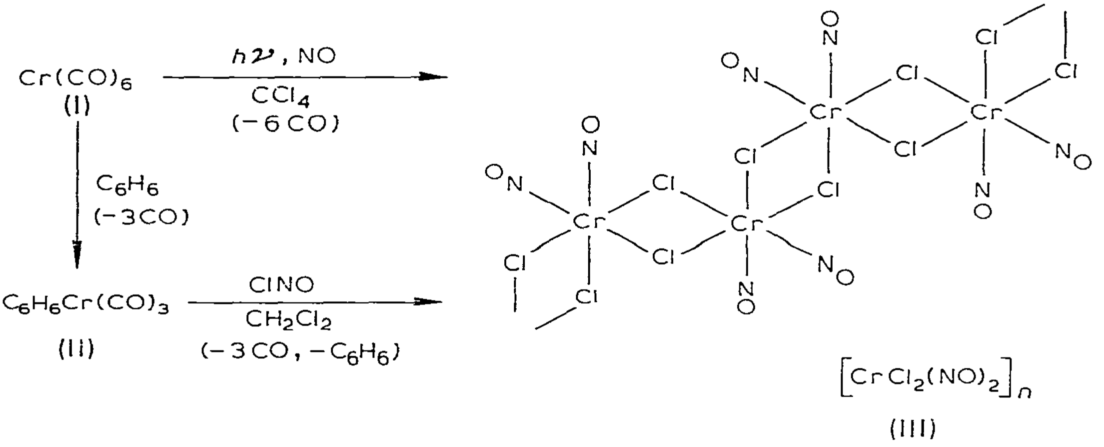
Although $Cr(CO)_6$ (I) in CCl_4 solution does not react with NO in the dark, a quantitative loss of all CO ligands takes place under photonitrosylation [16] conditions. The orange-brown product III precipitates from the solution.

A most convenient preparation of III involves the reaction of $C_6H_6Cr(CO)_3$ (II) with ClNO. In non-coordinating solvents such as hexane or dichloromethane, the yellow solution of II turns light-brown upon addition of ClNO (diluted with CH_2Cl_2), and III precipitates as an orange-brown powder.

$[CrCl_2(NO)_2]_n$ (III) is hygroscopic in the solid state. It readily dissolves in coordinating solvents (e.g. THF, alcohols, water and pyridine) but is almost insoluble in hydrocarbons, CCl_4 and CH_3NO_2. This behaviour indicates a polymeric structure containing chloro bridges which are split by potential ligands. According to the infrared spectrum (Table 1), the NO ligands are terminal and occupy *cis*-positions at the metal. A chloro-bridged, kinked chain of octahedrally coordinated chromium atoms appears to be the most plausible structure, as first proposed for $[MCl_2(NO)_2]_n$ (M = Mo, W) by Cotton and Johnson [5].

In the series of $[MCl_2(NO)_2]_n$ complexes (M = Cr, Mo, W), the chromium derivative differs remarkably from those of the higher homologues. The ν(NO) frequencies of III are higher (Table 1), and the orange-brown colour is in con-

SCHEME 1. PREPARATION OF DICHLORODINITROSYLCHROMIUM



trast to the dark green products obtained from the reactions of $M(CO)_6$ (M = Mo, W) with ClNO *.

B. Reaction of ArCr(CO)$_3$ with ClNO in tetrahydrofuran solution

While the oxidative decarbonylation of $C_6H_6Cr(CO)_3$ (II) with excess ClNO stops at the (insoluble) $[CrCl_2(NO)_2]_n$ (III) in CH_2Cl_2 solution, the reaction in THF eventually leads to $CrCl_3$:

$$C_6H_6Cr(CO)_3 + 3\ ClNO \xrightarrow[THF]{25^\circ C} CrCl_3 \cdot 3\ THF + C_6H_6 + 3\ CO + 3\ NO$$

By a suitable choice of temperature and molar ratios, all three steps in the redox process can be observed (Scheme 2). The identification of the two (solvent-stabilised) intermediates as $[CrCl(CO)_2(NO)] \cdot x$ THF (IV) and $[CrCl_2(NO)_2] \cdot y$ THF (V), respectively, is based on both the infrared spectra (in THF solution) and the derivatives prepared from these intermediates (Section D).

Addition of one equivalent ClNO to the THF solution of an $ArCr(CO)_3$ complex below −30° C leads to the red dicarbonylnitrosylchromium intermediate IV [17]. Elimination of the ring Ar in this first step is supported by the observation that the infrared spectrum of the solution (ν(CO) 2037, 1941; ν(NO) 1678 cm^{-1}) is independent of the nature of Ar in the starting complex $ArCr(CO)_3$ (Ar = benzene (II), *p*-substituted toluenes (XC_6H_4Me, X = F, OMe, NMe_2, Me), mesitylene, hexamethylbenzene, cycloheptatriene). The two CO ligands are lost if the THF solution is allowed to warm up to room temperature.

Addition of a second equivalent ClNO to the red solution of IV results in further oxidation to the brown dinitrosylchromium intermediate V (ν(NO) 1856, 1722 cm^{-1}). Solutions having the same infrared spectra are obtained

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* It has been pointed out [6,13], that $[WCl_2(NO)_2]_n$ tends to interact with ClNO and other materials. For example [6], the original green product obtained from $W(CO)_6$ and ClNO in CH_2Cl_2 solution readily loses ClNO under vacuum and is converted into a highly insoluble brown material having the (approximate) composition "$WCl_2(NO)_2$" and the reported [5] ν(NO) bands.

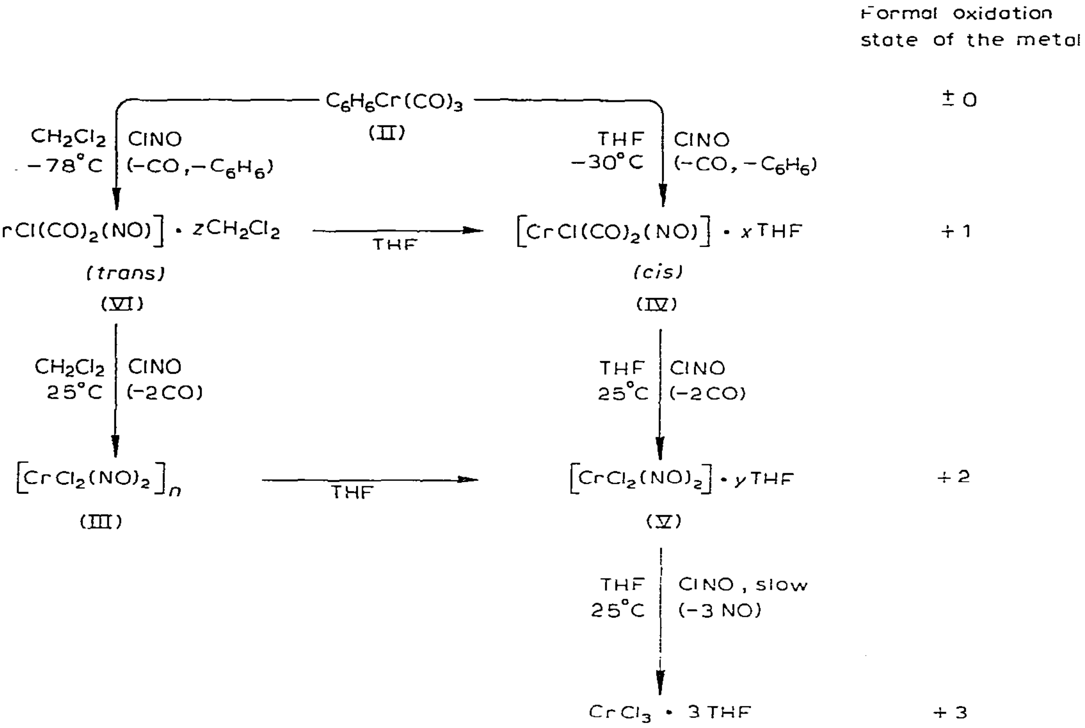
TABLE 1

INFRARED SPECTRA

Complex	Colour	ν(CO) (cm^{-1})	ν(NO) (cm^{-1})	Measured in	Ref.
$[CrCl_2(NO)_2]_n$ (III)	orange-brown		1871s, 1736s, (1610w) [b]	KBr	[a]
$[MoCl_2(NO)_2]_n$	dark green		1805s, 1690s, (1600w)	Nujol	[5]
$[WCl_2(NO)_2]_n$	dark green		1800s, 1680s, (1600w)	Nujol	[5]
$[ArCr(CO)_2(NO)]PF_6$					
Ar = C_6Me_6	yellow	2065, 2016	1758	CH_2Cl_2	[21]
Ar = $C_6H_3Me_3$		2073, 2027	1763	CH_2Cl_2	[20,21]
$[ArCr(CO)_2(NO)]Cl$					
Ar = C_6Me_6		2067, 2017	[c]	KBr	[a]
Ar = $C_6H_3Me_3$		2076, 2029	[c]	KBr	[a]
Ar = C_6H_6		2080, 2037	[c]	KBr	[a]
Intermediates:					
$[CrCl(CO)_2(NO)] \cdot x$ THF (IV)	red	2037, 1941	1678	THF	[a,d]
$[CrCl_2(NO)_2] \cdot y$ THF (V)	brown		1856, 1722	THF	[a]
$[CrCl(CO)_2(NO)] \cdot z$ CH_2Cl_2 (VI)	red	2075	1747	CH_2Cl_2	[e]

[a] This work. [b] Prepared by photonitrosylation of $Cr(CO)_6$ in CCl_4 solution. [c] Covered by the ν(NO) absorptions of the main product, III. [d] The frequencies given in the preliminary communication [17] have been corrected. [e] This work, cf. [18].

SCHEME 2. REACTION OF TRICARBONYLBENZENECHROMIUM (II) WITH NITROSYL CHLORIDE



when either two equivalents ClNO are added to a THF solution of $ArCr(CO)_3$ or the polymer $[CrCl_2(NO)_2]_n$ (III) is dissolved in THF.

In the presence of excess ClNO, the brown complex V in THF solution slowly loses its NO ligands as a result of further oxidation. The violet adduct $CrCl_3 \cdot 3$ THF eventually precipitates.

C. *Reaction of ArCr(CO)$_3$ with ClNO in dichloromethane solution*

The oxidative decarbonylation of $C_6H_6Cr(CO)_3$ (II) by ClNO in CH_2Cl_2 solution proceeds through a red intermediate (VI) which is converted into $[CrCl_2(NO)_2]_n$ (III). The highest concentration of VI (ν(CO) 2075, ν(NO) 1747 cm^{-1}) is reached when ca. 1.2 equivalents ClNO are added at —78° C: at this stage the bands of $C_6H_6Cr(CO)_3$ (II) (ν(CO) 1966, 1888 cm^{-1}) disappear while the absorptions of the (solvated) dichlorodinitrosylchromium (ν(NO) 1880, 1750 cm^{-1}) are still weak.

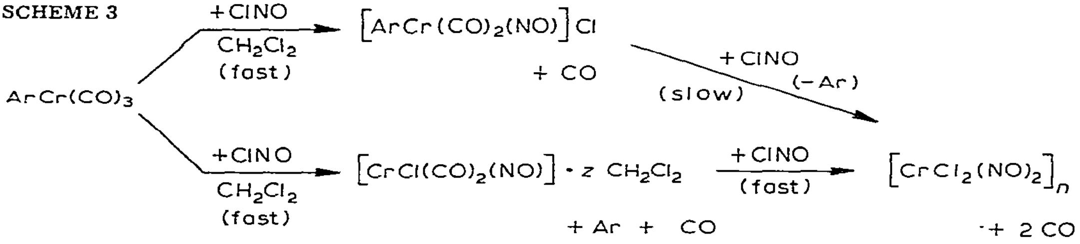
By analogy with the corresponding reaction in THF solution, intermediate VI was assigned the composition $[CrCl(CO)_2(NO)] \cdot z\ CH_2Cl_2$; since only a single ν(CO) absorption is observed, the CO ligands must be *trans* to each other. Addition of THF to the CH_2Cl_2 solution of VI changes the infrared spectrum to that of intermediate IV which contains a *cis*-dicarbonylchromium unit (Table 1). Addition of triethylphosphane, PEt_3, to the solutions of $[CrCl(CO)_2(NO)]$ in either CH_2Cl_2 or THF leads to the same adduct, $CrCl(CO)_2(NO)(PEt_3)_2$ [17], with both carbonyl and phosphane ligands in mutual *trans* positions. The primary loss of the π-bonded ring as a result of oxidative nitrosylation was demonstrated for the reaction of mesitylene tricarbonylchromium with ClNO: the CH_2Cl_2 solutions containing VI also show the ^1H NMR signals and the characteristic infrared absorption (at 1607 cm^{-1}) of free mesitylene.

Arene-free intermediates of the type $[CrCl(CO)_2(NO)]$ were first observed by Connelly et al. in the reaction of the hexamethylbenzene-containing cations $[C_6Me_6Cr(CO)_2(NO)]^+$ with chloride anions in CH_2Cl_2 solution; the initially formed *cis*-dicarbonyl species isomerises in the solution to the *trans*-dicarbonyl complex [18]. In the present study of the reaction of $ArCr(CO)_3$ (Ar = C_6H_6, $C_6H_3Me_3$, C_6Me_6) with ClNO, the *trans*-dicarbonyl intermediate VI is formed directly and almost exclusively.

It is remarkable that a different intermediate appears in the analogous reaction between $ArM(CO)_3$ (M = Mo, W) and ClNO in CH_2Cl_2 solution. According to Legzdins et al. [19], the green polymers $[MCl_2(NO)_2]_n$ are formed by decarbonylation of a red-brown precursor to which the composition $[MCl_2(CO)_2(NO)_2]$ was assigned on the basis of the infrared spectra (ν(CO) 2145, 2070, ν(NO) 1815, 1725 cm^{-1} when M = W).

Although elimination of the arene ligand, Ar, occurs easily when $ArCr(CO)_3$ complexes are oxidized by ClNO (Scheme 3), the formation of $[ArCr(CO)_2(NO)]^+$ cations is also possible in the case of methyl-substituted rings (e.g., Ar = mesitylene, hexamethylbenzene). The infrared spectrum of $[CrCl_2(NO)_2]_n$ (III), prepared from $C_6H_6Cr(CO)_3$ (II) and ClNO in CH_2Cl_2 solution, indicates the presence of an impurity having ν(CO) frequencies of equal intensity at 2080 and 2037 cm^{-1} (KBr). Increasing amounts of a similar dicarbonylchromium species are formed when the ring in the starting complex, $ArCr(CO)_3$, is varied in the order Ar = benzene < mesitylene < hexamethylbenzene. In the same series the ν(CO) frequencies decrease, indicating that the ring Ar must still be connected to the $[Cr(CO)_2]$ fragment (Table 1). The ν(CO) frequencies coincide, within experimental error, with those reported for the salts $[ArCr(CO)_2(NO)]PF_6$ (Ar = $C_6H_nMe_{6-n}$, n = 0—3) [20,21] (Table 1). The side product formed in addition to $[CrCl_2(NO)_2]_n$ (III) is therefore considered to be the salt $[ArCr(CO)_2(NO)]Cl$. Conversion of the salts $[C_6Me_6Cr(CO)_2(NO)]PF_6$ [20,21] and $[C_6Me_6Cr(CO)_2(NO)]Cl$ to III by excess ClNO takes place only very slowly in CH_2Cl_2 solution. This leads to the conclusion that the oxidation of $ArCr(CO)_3$ by ClNO can follow two different courses; the extent of cation formation depends on the nature of Ar and on the reaction conditions *.

SCHEME 3



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[*] The percentage of $ArCr(CO)_3$ converted to the salt $[ArCr(CO)_2(NO)]Cl$ in CH_2Cl_2 solution was estimated from the consumption of ClNO at the point where all starting $ArCr(CO)_3$ had just disappeared. For Ar = mesitylene and hexamethylbenzene, ca. 1.89 and 1.70 eq. ClNO were necessary, indicating about 11 and 30% salt formation.

D. Synthetic aspects

The oxidation of $C_6H_6Cr(CO)_3$ (II) by ClNO makes nitrosylchromium complexes generally accessible. The solvent-stabilised intermediates IV and VI (Scheme 2) lead to mononitrosylchromium derivatives, while the polymer $[CrCl_2(NO)_2]_n$ (III) is a convenient precursor for dinitrosylchromium compounds. Two reaction types have been studied: substitution of chloro ligands by anionic groups (A), and addition of two-electron ligands (L). Examples of chloride substitution include the reactions of $[CrCl(CO)_2(NO)] \cdot x$ THF (IV) with cyclopentadienyl-, indenyl- and fluorenyl-lithium to give $(A)Cr(CO)_2(NO)$ (A = cyclopentadienyl, indenyl and fluorenyl [17]), and the reactions of either $[CrCl_2(NO_2]_n$ (III) or $[CrCl_2(NO)_2] \cdot y$ THF (V) with dithiocarbamate salts to give *cis*-$[Cr(NO)_2(A)_2]$ (A = R_2NCS_2; R = Et [22], Me). The addition of two-electron ligands (L) to $[CrCl(CO)_2(NO)] \cdot x$ THF (IV) has been used to prepare complexes of the composition $CrCl(CO)_2(NO)L_2$ (L = pyridine, triethylphosphine; L_2 = 2,2′-bipyridine, 1,2-bis(diphenylphosphino)ethane); substitution of a CO group along with addition leads to $CrCl(CO)(NO)L_3$ (L = PMe_3, PMe_2Ph, $P(OMe)_3$) [17], respectively, while adducts of the type $CrCl_2(NO)_2L_2$ (L = *p*-toluidine, triphenylphosphane [23], triphenylphosphane oxide [24]) are now easily obtained by the reaction of $[CrCl_2(NO)_2]_n$ (III) with the potential ligands L. The scope of these reactions is presently being examined.

Experimental

Preparation of $[CrCl_2(NO)_2]_n$ (III)

(a) From $Cr(CO)_6$. A solution of 0.22 g (1 mmol) $Cr(CO)_6$ (I) in CCl_4 (200 ml) was irradiated for 90 min with a Hanovia L 450 W high-pressure mercury arc, while a slow stream of NO was bubbling through the reaction mixture. The disappearance of $Cr(CO)_6$ was followed in the infrared. The solvent was evaporated under vacuum, and the orange-brown powder of $[CrCl_2(NO)_2]_n$ (III) was dried for 2 h (100°C/0.1 Torr). Yield: 0.17 g (93%). This photonitrosylation method is restricted in scale because the product III is insoluble in CCl_4 and the reaction mixture then no longer absorbs sufficient light for further reaction.

(b) From $C_6H_6Cr(CO)_3$. A solution of ClNO in CH_2Cl_2 (12 ml, 6.6 mmol) was added to a stirred solution of $C_6H_6Cr(CO)_3$ (II) (0.64 g, 3 mmol) in CH_2Cl_2 (20 ml). Gas evolved, and an orange-brown precipitate of III was formed. The solvent was removed under vacuum, and the residue III was washed with hexane and dried for 2 h (100°C/0.1 Torr). Yield 0.50 g (91%).

Reactions of $ArCr(CO)_3$ (Ar = benzene, mesitylene, hexamethylbenzene) with ClNO in THF solution

(a) cis-$[CrCl(CO)_2(NO)] \cdot x$ THF (IV). A stirred solution of 1.5 mmol $ArCr(CO)_3$ (e.g., 0.45 g $C_6Me_6Cr(CO)_3$) in 20 ml THF was cooled below −30°C and treated with a solution of ClNO in THF (2 ml, 1.5 mmol). Gas evolved, and the yellow solution turned red. The infrared spectrum (Table 1) indicated the presence of IV. The complex gradually lost the CO ligands when the solution warmed up to ambient temperature [17].

(b) $[CrCl_2(NO)_2] \cdot y$ THF (V). A solution of ClNO in THF (4 ml, 3 mmol) was added to a stirred solution of 1.5 mmol $ArCr(CO)_3$ (e.g., 0.38 g

$C_6H_3Me_3Cr(CO)_3$) in 20 ml THF at room temperature. Gas evolution occurred, and the solution turned brown. The intermediate formation of IV is not observed unless the reaction is carried out stepwise at low temperature.

(c) $CrCl_3 \cdot 3$ THF. A solution of 1.5 mmol $ArCr(CO)_3$ (e.g., 0.32 g $C_6H_6Cr(CO)_3$) in 20 ml THF was treated with a solution of ClNO in THF (6 ml, 4.5 mmol) at room temperature. Rapid gas evolution (CO) took place. When the brown solution was further stirred for 0.5 h, the gas evolution (NO) continued smoothly and a violet solid precipitated. The solvent was removed in vacuo, and the violet residue was washed with hexane and dried 1 h in vacuo. Yield 0.53 g (95%) $CrCl_3 \cdot 3$ THF.

Acknowledgments

The work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We especially thank W. Kremnitz for experimental assistance, and Prof. B.R. Willeford for helpful discussions.

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