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Insertion Reactions into the Chromium-Carbon σ Bond of h^5-$C_5H_5Cr(NO)_2R$

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A study is reported on reactions between h^5-$C_5H_5Cr(NO)_2R$ *(R =* CH_3 *and* $CH_2C_6H_5$*) and each of the following unsaturated molecules: CO, SCO,* SO_2*, and* $(CN)_2C{=}C(CN)_2$*. Carbon monoxide and carbonyl sulfide do not insert into the Cr–*CH_3 *bond of* h^5-$C_5H_5Cr(NO)_2CH_3$ *at room temperature (SCO) and in hexane or THF at reflux (CO). Sulfur dioxide inserts readily into these Cr–R bonds to yield stable, crystalline S-sulfinato complexes,* h^5-$C_5H_5Cr(NO)_2S(O)_2R$ *(R =* CH_3 *and* $CH_2C_6H_5$*). Tetracyanoethylene furnishes* h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2CH_3$ *with* h^5-$C_5H_5Cr(NO)_2CH_3$*, and both* h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2CH_2C_6H_5$ *and* h^5-$C_5H_5Cr(NO)_2N{=}C{=}C(CN)C(CN)_2CH_2C_6H_5$ *with* h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$*. Spectroscopic evidence exists that* h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2R$ *(R =* CH_3 *or* $CH_2C_6H_5$*) isomerizes slowly to* h^5-$C_5H_5Cr(NO)_2N{=}C{=}C(CN)C(CN)_2R$ *in* CH_2Cl_2 *solution.*

Introduction

Insertion reactions are known to play a prominent role in synthetic and catalytic organometallic chemistry.[1–5] Many studies on such reactions have been carried out with transition metal alkyl carbonyls, e.g., $Co(CO)_4R$, $Mn(CO)_5R$, h^5-$C_5H_5Fe(CO)_2R$, and h^5-$C_5H_5Mo(CO)_3R$. They have shown that the so-called carbon monoxide insertion is an intramolecular process which proceeds by migration of R onto a coordinated CO.[3] However, insertion of other unsaturated molecules into a metal–carbon bond is not nearly as well understood as that of CO.

In order to learn more about the role of coordinated CO in various insertion processes we have endeavored to examine the behavior toward unsaturated compounds of the Cr–R bond in h^5-$C_5H_5Cr(NO)_2R$. This alkyl nitrosyl system is isoelectronic with the well-studied[4,6–9] h^5-$C_5H_5Fe(CO)_2R$. Therefore, we expected it to provide an interesting and useful model for comparison of the effects of coordinated NO vs. coordinated CO on the insertion of various types of unsaturated molecules. Reported herein are our results on the insertion of four compounds – CO, SO_2, $(CN)_2C{=}C(CN)_2$ (TCNE), and SCO – into the Cr–R bond of h^5-$C_5H_5Cr(NO)_2R$.

Experimental

General Procedures

A nitrogen atmosphere was employed routinely for all of the reactions reported herein. Chromatographic separations and purifications were effected using Ventron alumina deactivated with H_2O (6–10% unless otherwise indicated). Elemental analyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany, and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements

Infrared spectra were recorded on a Perkin–Elmer Model 337 spectrophotometer. Hydrogen-1 nmr spectra were obtained on a Varian Associates A–60 or A–60A spectrometer using tetramethylsilane as an internal standard. Molecular weight measurements were made on *ca.* $1 \times 10^{-2} M$ $CHCl_3$ solutions with a Mechrolab Model 301–A osmometer by Dr. M. A. Jennings. Melting points were taken in sealed capillaries immersed in a mineral oil bath and are uncorrected.

Materials

Anhydrous grade SO_2, from Matheson, was passed through concentrated H_2SO_4 and a P_4O_{10}–$CaCl_2$ column before condensation. Nitric oxide and carbonyl sulfide (SCO), also from Matheson, were used as received. Carbon monoxide and chlorine were purchased from J. T. Baker and Co. and used without further purification. TCNE, procured from Aldrich Chemical Co., was sublimed prior to use. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. Diethyl ether was purified by distillation from CaH_2. All other chemicals and solvents were reagent grade or equivalent.

The complex h^5-$C_5H_5Cr(NO)_2Cl$ was prepared as described by King.[10] The corresponding iodide, h^5-$C_5H_5Cr(NO)_2I$, was obtained by a literature procedure,[11] but from h^5-$C_5H_5Cr(NO)_2Cl$ rather than h^5-$C_5H_5Cr(NO)_2Br$. After purification by chromatography on alumina, the desired product was isolated in 34% yield. The methyl derivative h^5-$C_5H_5Cr(NO)_2CH_3$[11] resulted from treatment of h^5-$C_5H_5Cr(NO)_2Cl$ with

CH_3MgI; it was purified by chromatography on alumina using pentane eluent and isolated in 58% yield. Its benzyl analog, h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$, was synthesized by a similar procedure which is outlined below.

The Grignard reagent from 2 g (0.08 mol) of Mg turnings and 10 g (0.08 mol) of benzyl chloride in 50 ml of diethyl ether was added dropwise to 7.1 g (0.033 mol) of h^5-$C_5H_5Cr(NO)_2Cl$ in 400 ml of diethyl ether. Stirring was continued for *ca.* 2.5 hr. The solvent was then evaporated (20 Torr, 25°), the residue was extracted with pentane, and the extract was filtered through Zeolite. The clear solution was concentrated in a stream of nitrogen and then chromatographed on alumina eluting with pentane. The single band which had developed was collected and the solvent was removed in a stream of nitrogen to give 3.7 g (41%) of olive green platelets, m.p. 54–57° (dec.). Anal. Calcd. for $C_{12}H_{12}N_2O_2Cr$: C, 53.73; H, 4.51. Found: C, 53,57; H, 4.44. Ir (cm^{-1}, $CHCl_3$ soln.) 1780 vs, 1670 vs (ν_{NO}); nmr (τ, $CDCl_3$ soln.) 6.95 s (CH_2), 4.69 s (C_5H_5), 2.87 m (C_6H_5).

Reactions of h^5-$C_5H_5Cr(NO)_2R$ (R = CH_3 and $CH_2C_6H_5$) with SO_2

The alkyl complex (0.25–0.50 g) was dissolved in liquid SO_2 (25 ml) and the resulting solution was kept at reflux for 15–31 hr.[12] Removal of the SO_2 and chromatography on alumina using CH_2Cl_2 or $CHCl_3$ eluent afforded h^5-$C_5H_5C^{-}(NO)_2S(O)_2CH_3$ in 42% yield and h^5-$C_5H_5Cr(NO)_2S(O)_2CH_2C_6H_5$ in 62% yield.

The two *S*-sulfinato complexes have been also obtained by dissolving the corresponding alkyls (0.2–0.5 g) in hexane (50 ml) at room temperature and passing SO_2 into the resulting solution for 7 (R = CH_3) or 24 hr (R = $CH_2C_6H_5$). Evaporation of the solvent and chromatography of the dissolved (CH_2Cl_2 or $CHCl_3$) residue furnished h^5-$C_5H_5Cr(NO)_2S(O)_2CH_3$ quantitatively and h^5-$C_5H_5Cr(NO)_2S(O)_2CH_2C_6H_5$ in 35% yield (16% unreacted h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$ was recovered from the first chromatographic band). Analytical data and physical properties of these and other new insertion products of h^5-$C_5H_5Cr(NO)_2R$ are presented in Table I.

Attempts at Desulfination of h^5-$C_5H_5Cr(NO)_2S(O)_2CH_2C_6H_5$

The *S*-sulfinato complex was dissolved in benzene or in toluene and the resulting solution was maintained at reflux. Continuous monitoring of the solution by infrared spectroscopy showed no evidence of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$; extensive decomposition was noted as the refluxing continued.

In another experiment, 0.75 g of h^5-$C_5H_5Cr(NO)_2S(O)_2CH_2C_6H_5$ in 150 ml of benzene was irradiated for 30 min with a Hanovia 450–W high-pressure quartz mercury vapor lamp, Model 679 A–36, as described elsewhere.[13] The infrared spectrum of the reaction mixture showed no evidence of desulfination. Some (43%) *S*-sulfinato complex was recovered after chromatography of the irradiated solution.

Reactions of h^5-$C_5H_5Cr(NO)_2R$ (R = CH_3 and $CH_2C_6H_5$) with TCNE

(i) h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$

A solution of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$ (0.50 g, 1.9 mmol) in 50 ml of CH_2Cl_2 was treated with 0.40 g (3.1 mmol) of TCNE. The mixture was stirred at room temperature while progress of the reaction was checked by infrared spectroscopy (change in ν_{NO}). After *ca.* 0.75 hr solvent was removed, the dark solid was treated with $CHCl_3$, and the mixture was filtered to remove excess TCNE. The resultant green solution was concentrated and chromatographed on alumina eluting with $CHCl_3$. A black and a red band appeared at the top of the column but could not be eluted off. Three bands were collected.

The green solution of band 1 was concentrated in a stream of nitrogen and rechromatographed on alumina (3% H_2O). Evaporation of the solvent afforded 0.10 g (13% yield) of a compound, m.p. 103–104° (dec.), analyzing as a 1 : 1 adduct of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$ and TCNE (designated as isomer 1). The solution of band 2 was also concentrated and rechromatographed on alumina (3% H_2O) using $CHCl_3$ eluent. Concentration in a stream of nitrogen and addition of pentane furnished shiny golden-brown crystals of isomer 2 of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5 \cdot$TCNE (0.07 g, 10% yield),

TABLE I. Analytical Data and Physical Properties of Insertion Products of h^5-$C_5H_5Cr(NO)_2R$.

Compound	Analysis, % C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found	Mol. wt. Calcd.	Mol. wt. Found	Color
h^5-$C_5H_5Cr(NO)_2S(O)_2CH_3$	28.13	28.13	3.15	3.13					deep green
h^5-$C_5H_5Cr(NO)_2S(O)_2CH_2C_6H_5$	43.37	42.94	3.64	3.55					deep green
h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2CH_3$	45.01	44.73	2.52	2.52	26.24	26.06	320	346	green
h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2CH_2C_6H_5$[a]	54.55	54.57	3.05	2.98	21.20	21.53	396	431	green
h^5-$C_5H_5Cr(NO)_2N{=}C{=}C(CN)C(CN)_2CH_2C_6H_5$[b]	54.55	53.49	3.05	3.02	21.20	20.54	396	404	golden-brown

[a] Designated as isomer 1. [b] Designated as isomer 2.

m.p. 79–80° (dec.). Band 3 yielded 0.04 g (10%) of the known[14,15] h^5-$C_5H_5Cr(NO)_2CN$ after an additional chromatography (alumina, 3% H_2O) and removal of the solvent.

After the same reaction had been carried out in THF for 5–6 hr and the resulting mixture chromatographed on alumina, isomer 2 was eluted off first (35% yield), followed by two other bands which could not be effectively separated. Their infrared spectra showed presence of some h^5-$C_5H_5Cr(NO)_2CN$. Isomer 1 was not detected among the products.

(ii) h^5-$C_5H_5Cr(NO)_2CH_3$

A solution of h^5-$C_5H_5Cr(NO)_2CH_3$ (0.70 g, 3.6 mmol) in 100 ml of THF was treated with TCNE (0.77 g, 6.0 mmol) in 10 ml of THF. The mixture was stirred at room temperature until the infrared ν_{NO} bands of the alkyl complex had disappeared (48–72 hr). Solvent was then removed, the dark green oil was dissolved in $CHCl_3$, and the resulting solution was filtered. Concentration in a stream of nitrogen and chromatography using $CHCl_3$ eluent gave rise to the appearance of four bands. The last band decomposed in the course of the elution.

Band 1 afforded a minute amount of a yellow oil which showed no infrared ν_{CN} absorptions. The oil decomposed after a short storage. The solution from band 2 was concentrated and rechromatographed (alumina, 3% H_2O). Evaporation of the $CHCl_3$ and washing with pentane yielded 20–40% of bright green crystals of h^5-$C_5H_5Cr(NO)_2CH_3 \cdot TCNE$, m.p. 67–68° (dec.). Spectroscopic properties *(vide infra)* showed this material to be analogous to isomer 1 of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5 \cdot TCNE$. Band 3 was comprised of more than one compound. A small amount of h^5-$C_5H_5Cr(NO)_2CN$ was isolated therefrom after repeated chromatography and crystallization.

This reaction has been also conducted in CH_2Cl_2. Removal of the solvent after 3 hr and chromatography on alumina led to the appearance of four bands. Bands 1 and 3 furnished yellow oils whereas band 4 gave a red oil. These three oils showed infrared ν_{NO}(1840–1830 and 1742–1730 cm^{-1}) and ν_{CN}(2207–2133 cm^{-1}) absorptions but could not be characterized because of low stability and small amounts available. After several purifications on alumina (3 and 6% H_2O), band 2 yielded *ca.* 40% of green crystalline h^5-$C_5H_5Cr(NO)_2CH_3$ TCNE which was identical with the sample obtained from the reaction conducted in THF.

Subsequent attempts at reproduction of the preceding results (CH_2Cl_2 solvent only) have met with mixed success; on some occasions, no h^5-$C_5H_5Cr(NO)_2CH_3 \cdot TCNE$ could be isolated.

Isomerization Reactions of h^5-$C_5H_5Cr(NO)_2R$ · TCNE

A solution of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5 \cdot TCNE$ (isomer 1) in CH_2Cl_2 was examined periodically in the ν_{CN} infrared region. After 12 hr, absorptions were observed at 2202sh and 2145m cm^{-1}, in addition to that of the starting compound at 2223m cm^{-1}. After 60 hr, the first two bands have gained intensity at the expense of the 2223-cm^{-1} band.

The infrared spectrum of isomer 2 of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5 \cdot TCNE$ in CH_2Cl_2 remained unchanged after storage for 80 hr.

A solution of h^5-$C_5H_5Cr(NO)_2CH_3 \cdot TCNE$ in CH_2Cl_2, stored at room temperature, was also examined periodically by infrared spectroscopy. After 63 hr, new absorptions were noted at 2212w, 2167w, and 2150m cm^{-1}. Apart from some loss in intensity owing to decomposition, the spectrum remained essentially constant after this period.

Reactions of h^5-$C_5H_5Cr(NO)_2CH_3 \cdot TCNE$ with the Halogens

To a solution of 0.2 g (0.6 mmol) of h^5-$C_5H_5Cr(NO)_2CH_3 \cdot TCNE$ in 10 ml of benzene was added 0.02 g (0.8 mmol) of I_2 and a trace of KI. The mixture was stirred for 48 hr, solvent was removed, and the residue was dissolved in $CHCl_3$ and chromatographed on alumina. The three bands that had developed yielded, respectively, on elution: (1) a pale yellow solution (no ν_{NO} or ν_{CN} infrared absorptions), (2) starting metal complex (50% recovery), and (3) a yellow solution showing infrared bands at 2218, 2201, 2162, 2139, 1820, and 1719 cm^{-1} which was not characterized. None of the expected h^5-$C_5H_5Cr(NO)_2I$ was obtained.

A similar treatment of the title compound with Br_2 in THF led to some recovery of the metal nitrosyl. Chlorine, on the other hand, decomposed h^5-$C_5H_5Cr(NO)_2CH_3 \cdot TCNE$ in THF to a tan solid, insoluble in $CHCl_3$, which was not characterized. In neither case was there any evidence for the formation of h^5-$C_5H_5Cr(NO)_2X$.

Reactions of h^5-$C_5H_5Cr(NO)_2X$ (X = Cl and I) with TCNE

Treatment of h^5-$C_5H_5Cr(NO)_2Cl$ (0.50 g, 2.4 mmol) in 50 ml of CH_2Cl_2 with 0.88 g (6.9 mmol) of TCNE at room temperature for 48 hr afforded after chromatography on alumina (1) the unreacted chloro complex and (2) h^5-$C_5H_5Cr(NO)_2CN$ (0.08 g, *ca.* 20% yield).

Similarly, reaction between h^5-$C_5H_5Cr(NO)_2I$ and TCNE in THF at room temperature for 72 hr gave 76% unreacted iodo complex and an undetermined amount of the corresponding cyano complex (characterized by the infrared ν_{CN} and ν_{NO} absorptions).

Attempts at Carbonylation of h^5-$C_5H_5Cr(NO)_2CH_3$

Carbon monoxide was passed into a solution of h^5-$C_5H_5Cr(NO)_2CH_3$ (0.5 g) in hexane (50 ml) at room temperature. After 20 hr the reaction was discontinued and the solvent was removed. Only the starting material was detected in the residue by infrared spectroscopy.

When the above reaction was carried out in hexane at reflux for 28 hr, the solution changed color from green to yellow–brown. Cooling to room temperature, removal of the solvent, and chromatography on alumina eluting with CH_2Cl_2 afforded only the starting methyl complex. There was no infrared spectroscopic evidence (e.g., acetyl ν_{CO}) for h^5-$C_5H_5Cr(NO)_2C(O)CH_3$.

Similarly, the alkyl compound was recovered (94%) after treatment with CO in THF at reflux for 24 hr.

Attempted Reaction of h^5-$C_5H_5Cr(NO)_2CH_3$ with SCO

Into a solution of h^5-$C_5H_5Cr(NO)_2CH_3$ (0.5 g) in THF (50 ml) at room temperature carbonyl sulfide was bubbled for 21 hr. The solvent was then removed and the residue was dissolved in CH_2Cl_2 and chromatographed on alumina. The only band that had developed was shown by infrared spectroscopy to contain the unreacted title complex.

Results and Discussion

Insertion Reactions of h^5-$C_5H_5Cr(NO)_2R$

The complexes h^5-$C_5H_5Cr(NO)_2R$ (R = CH_3 and $CH_2C_6H_5$) have been treated with four unsaturated molecules possessing potential capability of inserting into a metal-carbon bond. These molecules are CO, SCO, SO_2, and TCNE. Their reactions with h^5-$C_5H_5Cr(NO)_2R$ will be taken up in the above-indicated order.

Treatment of h^5-$C_5H_5Cr(NO)_2CH_3$ with CO in hexane or THF at reflux led to a partial recovery of the chromium methyl complex. There was no evidence of formation of h^5-$C_5H_5Cr(NO)_2C(O)CH_3$. This result further emphasizes the importance of coordinated CO, onto which the R group migrates,[3] in the carbon monoxide insertion reaction. Such coordination of CO to the metal is prevented here by the coordinative saturation of chromium in h^5-$C_5H_5Cr(NO)_2CH_3$. Carbon monoxide insertion also does not occur with h^5-$C_5H_5Ni(PR_3)R'$ (R = n-C_4H_9 and C_6H_5, R' = CH_3; R = R' = C_6H_5),[16,17] no doubt for reasons similar to that given above.

Although carbonyl sulfide, SCO, is known to insert into the Sn–P bond of $(C_6H_5)_3SnP(C_6H_5)_2$,[18] no examples have been reported of its insertion into metal–carbon linkages. We find in this study that there is no reaction between h^5-$C_5H_5Cr(NO)_2CH_3$ and SCO in THF at ambient conditions. The significance of this result will have to await further investigations on the propensity toward the insertion of SCO.

Sulfur dioxide reacts readily with h^5-$C_5H_5Cr(NO)_2CH_3$ and h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$ either as a neat liquid or in hexane solution to yield 1:1 adducts formulated *(vide infra)* as the *S*-sulfinates, h^5-$C_5H_5Cr(NO)_2S(O)_2CH_3$ and h^5-$C_5H_5Cr(NO)_2S(O)_2CH_2C_6H_5$, respectively. From recent results of a study on the reaction of SO_2 with various h^5-$C_5H_5Fe(CO)_2R$ complexes[19] it seems likely that the insertion in h^5-$C_5H_5Cr(NO)_2R$ proceeds *via* the intermediacy of the corresponding *O*-sulfinates, h^5-$C_5H_5Cr(NO)_2OS(O)R$. However, no attempt was made to detect such an intermediate in this work. The occurrence of the SO_2 reaction with h^5-$C_5H_5Cr(NO)_2R$ as well as with the isoelectronic h^5-$C_5H_5Fe(CO)_2R$[13] is in complete accord with the proposed pathway for this insertion.[8] Neither the coordinated CO nor the coordinated NO is actively involved in the mechanism.

The reaction between h^5-$C_5H_5Cr(NO)_2R$ (R = CH_3 and $CH_2C_6H_5$) and TCNE in CH_2Cl_2 or THF at room temperature is complex and affords several products. Complete characterization of some of these products was precluded by one or more of the following factors: small size of the isolated sample, inherent instability, and difficulty of purification. Three types of the chromium nitrosyl complex were satisfactorily characterized *(vide infra)*. They comprise two isomeric insertion products, h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2R$ and h^5-$C_5H_5Cr(NO)_2N{=}C{=}C(CN)C(CN)_2R$ (only the former could be isolated when R = CH_3), and the cyano derivative h^5-$C_5H_5Cr(NO)_2CN$. The last compound was probably formed as a result of the scission of the Cr–R bond by HCN or through decomposition of one or both of the isomeric insertion products.

The aforementioned reaction was found to proceed more rapidly with h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$ than with h^5-$C_5H_5Cr(NO)_2CH_3$. This observation is noteworthy since the above reactivity order of the two complexes toward TCNE is opposite of that observed toward SO_2 in hexane. Furthermore, transition metal methyl complexes, e.g., h^5-$C_5H_5Fe(CO)_2CH_3$, $Mn(CO)_5CH_3$, etc., generally undergo insertion reactions considerably faster than do their benzyl analogs.[3,8,20] The more facile insertion in h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5$ than in h^5-$C_5H_5Cr(NO)_2CH_3$ may be a reflection of a free radical mechanism. Such a mechanism likely operates in the insertion of O_2 into the Co–R bond in $RCo(dmgH)_2py$ (dmgH = dimethylglyoximato), where benzylic complexes react more readily than the alkyl complexes.[21] Unfortunately, the reaction of TCNE with h^5-$C_5H_5Cr(NO)_2R$ is not sufficiently clean to be amenable to a kinetic study which could resolve this point.

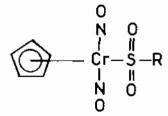
Of the two solvents employed for the insertion, THF and CH_2Cl_2, the latter proved to accelerate substantially the rate of the reaction when compared with the former. The reason for this is not obvious to us at present. Both solvents have comparable dielectric constants: $\varepsilon = 7.70$ for THF[22] and 9.08 for CH_2Cl_2.[23] In spite of the faster insertion in CH_2Cl_2, this solvent is sometimes less desirable than THF on account of the problems which were described in the Experimental.

TCNE also reacts with h^5-$C_5H_5Fe(CO)_2R$ to furnish analogous isomeric insertion products.[24,25] Thus, again, the coordinated CO or NO in the metal alkyl complex appears to play no direct role in the insertion.

Characterization and Properties of Insertion Products

The new chromium complexes derived by insertion of SO_2 or TCNE into the Cr–R bond of h^5-$C_5H_5Cr(NO)_2R$ are green or golden-brown crystalline solids. With the exception of isomer 2 of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5 \cdot$TCNE, they are very stable to air at room temperature. Isomer 2 of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5 \cdot$TCNE is somewhat less stable in this respect. All of the compounds are soluble in polar organic solvents, but insoluble in nonpolar solvents.

The infrared and ^1H nmr spectra of the new complexes are listed in Table II. The SO_2-containing products show ν_{SO} absorptions at 1195–1194 and 1053 cm^{-1}. These frequencies are in the range expected for metal *S*-sulfinato complexes;[26] they thus provide good evidence for the proposed mode of metal–ligand attachment. In further support of the assigned structure (I), the CH_3 protons in h^5-$C_5H_5Cr(NO)_2S(O)_2CH_3$ and the CH_2 protons in h^5-$C_5H_5Cr(NO)_2S(O)_2CH_2C_6H_5$ absorb at much lower fields (τ 6.95 and 5.67) than in their alkyl precursors (τ 9.42 and 6.95, respectively).



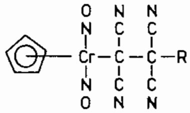
I

Comparable shifts have been noted upon insertion of SO_2 into h^5-$C_5H_5Fe(CO)_2R$ (R = CH_3 and $CH_2C_6H_5$).[13] Finally, the values of ν_{NO} of the *S*-sulfinato complexes are 40–61 cm^{-1} higher than those of the parent alkyls. A comparable change in ν_{CO} occurs on going from h^5-$C_5H_5Fe(CO)_2R$ to h^5-$C_5H_5Fe(CO)_2S(O)_2R$.[13]

The chromium *S*-sulfinates resist loss of SO_2 either upon thermolysis in benzene or toluene at reflux or upon photolysis in benzene. Such resistance to desulfination has been noted for other transition metal *S*-sulfinato complexes.[4,26]

Isomer 1 of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5 \cdot$TCNE and h^5-$C_5H_5Cr(NO)_2CH_3 \cdot$TCNE show the nmr CH_2 and CH_3 proton resonances at τ6.29 and 7.72, respectively. These signals occur considerably downfield from those for the respective alkyl precursors and point to insertion of TCNE into the Cr–R bond. The C_5H_5 protons of the two products (τ 4.10 and 4.12) also experience a substantial deshielding compared to those of the parent alkyls (τ 4.69 and 4.63, respectively). The position of the two ν_{NO} absorptions (1837–1830 and 1736–1730 cm^{-1}) is 53–66 cm^{-1} higher than that for the appropriate h^5-$C_5H_5Cr(NO)_2R$, reflecting considerable withdrawal of electrons from the metal by the newly formed ligand TCNE·R. Both products show a weak ν_{CN} absorption at 2225–2217 cm^{-1} in their infrared spectra.

The aforementioned spectroscopic data point to the structure (*cf* II) derived by 1,2-addition of Cr–R to the C=C bond of TCNE. This assignment receives further support from the position of the CH_2 proton resonance of h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2CH_2C_6H_5$ (τ 6.29) which is close to that of the CH_2 resonances in $(C_6H_5)_2\overline{CCH_2\mathit{CH}_2C(CN)_2C}(CN)_2$ (τ 6.88),[27] $C_6H_5\mathit{CH}_2C(CN)_2H$ (τ 6.78)[28], and h^5-$C_5H_5Fe(CO)_2\overline{C(CH_3)\mathit{CH}_2C(CN)_2C(CN)_2\mathit{CH}_2}$ (τ 6.98 and 6.62).[29] Also consistent with the proposed structure of these products is



II

TABLE II. Infrared and Proton Magnetic Resonance Spectra of Insertion Products of h^5-$C_5H_5Cr(NO)_2R$.

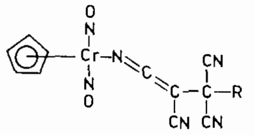
Compound	Ir, cm^{-1}			Nmr, τ^c	
	$\nu_{CN}{}^a$	$\nu_{NO}{}^a$	$\nu_{SO}{}^b$	C_5H_5	Other protons
h^5-$C_5H_5Cr(NO)_2S(O)_2CH_3$		1825 vs, 1731 vs	1194 s, 1053 s	4.17 s	6.95 s (CH_3)
h^5-$C_5H_5Cr(NO)_2S(O)_2CH_2C_6H_5$		1820 vs, 1725 vs	1195 s, 1053 s	4.25 s	5.67 s (CH_2) 2.55 m (C_6H_5)
h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2CH_3$	2217 w	1831 vs, 1730 vs		4.12 s	7.72 s (CH_3)
h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2CH_2C_6H_5{}^d$	2225 w	1837 vs, 1736 vs		4.10 s	6.29 s (CH_2) 2.45 s, br (C_6H_5)
h^5-$C_5H_5Cr(NO)_2N{=}C{=}C(CN)C(CN)_2CH_2C_6H_5{}^e$	2212 m, 2156 s^f, 1293 m^g	1837 vs, 1736 vs		4.24 s	6.68 s (CH_2) 2.46 s, br (C_6H_5)

[a] In $CHCl_3$ solution. [b] In Nujol mull. Abbreviations: vs, very strong; s, strong; m, medium; w, weak. [c] In $CDCl_3$ solution. Abbreviations: s, singlet; m, multiplet; br, broad. [d] Designated as isomer 1. [e] Designated as isomer 2. [f] $\nu_{N=C=C}$(antisym.). [g] $\nu_{N=C=C}$(sym.).

the observation that the chromium nitrosyl halides h^5-$C_5H_5Cr(NO)_2X$ (X = Cl and I) failed to give analogous complexes upon reaction with TCNE. This suggests that the Cr–R bond is the reactive center in the chromium alkyls.

Attempts were made to cleave the Cr–C bond in h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2CH_3$ with I_2, Br_2, and Cl_2 to obtain further evidence for the assigned structure. However, results of these experiments proved inconclusive.

A salient feature in the infrared spectrum of isomer 2 of h^5-$C_5H_5Cr(NO)_2CH_2C_6H_5 \cdot$TCNE is the appearance of a strong absorption at 2156 cm^{-1} and a medium-intensity one at 1293 cm^{-1}. This indicates presence of a metal–keteniminato linkage, M–N=C=C (structure III). For comparison, keteniminato complexes of formula h^5-$C_5H_5Fe(CO)_2N{=}C{=}C(CN)C(CN)_2R$ show the two N=C=C stretching modes at 2162–2140 and 1306–1295 cm^{-1},[24,25] whereas $Ir(CO)(TCNE)[P(C_6H_5)_3]_2N{=}C{=}C(CN)C(CN)_2H$, whose structure was elucidated crystallographically, absorbs at 2168 and 1355 cm^{-1}.[30]



III

To test for possible interconversion between structures II and III, solutions of the three isolated TCNE-containing complexes in CH_2Cl_2 were examined periodically in the ν_{CN} infrared region. Evidence was obtained for slow isomerization of h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2CH_2C_6H_5$ to h^5-$C_5H_5Cr(NO)_2N{=}C{=}C(CN)C(CN)_2CH_2C_6H_5$ and, possibly, of h^5-$C_5H_5Cr(NO)_2C(CN)_2C(CN)_2CH_3$ to h^5-$C_5H_5Cr(NO)_2N{=}C{=}C(CN)C(CN)_2CH_3$. However, a solution of h^5-$C_5H_5Cr(NO)_2N{=}C{=}C(CN)C(CN)_2CH_2C_6H_5$ in CH_2Cl_2 remained unchanged after storage for 80 hr. It is noteworthy that several metal carbonyl *S*-thiocyanato complexes also isomerize to the thermodynamically more stable *N-thiocyanato analogs.*[31]

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