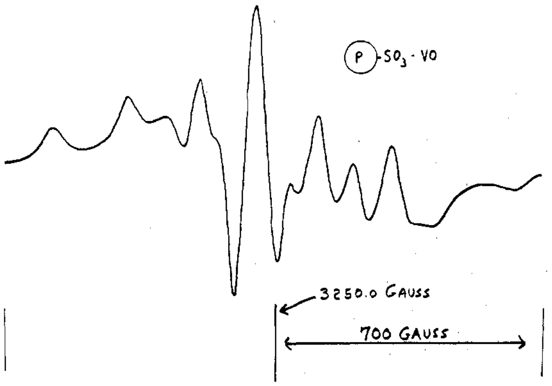

Figure 1. First-derivative ESR spectrum of the resin-bound VO^{2+} catalyst before and after a 6-h oxidation reaction.

The ESR data suggest either that the catalytically active species is VO^{2+}, and not V(V), for the resin-bound system or that the oxidation state change on the metal is reversible. However, it is also possible that only a tiny fraction of the vanadium sites are catalytically active, and the spectrum obtained after reaction merely arises from the inactive sites. If this latter possibility is correct, then the resin-bound catalyst which shows about a sixfold increase in activity over the homogeneous system is actually far more active than that, since the reaction would be promoted by considerably fewer catalytic sites.

We are not yet in a position to differentiate among the possible explanations; the answer must await further studies on the active form of the catalytic species.

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Registry No. *tert*-Butyl hydroperoxide, 75-91-2; cyclohexene, 110-83-8; 1-methylcyclohexane, 591-49-1; 1,2-dimethylcyclohexene, 1674-10-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; 1-hexene, 592-41-6; *cis*-2-hexene, 7688-21-3; *trans*-3-hexene, 13269-52-8; 1-octene, 111-66-0; 2,4,4-trimethyl-1-pentene, 107-39-1; 2,4,4-trimethyl-2-pentene, 107-40-4; *cis*-3-methyl-2-hexene, 10574-36-4; VO^{2+}, 20644-97-7.

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Organometallic Nitrosyl Chemistry. 4.[1] Additional Reactions of Nitrosyl Chloride with Neutral Carbonyl Complexes

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Nitrosyl chloride exhibits a number of different reaction modes during its reactions with monomeric and dimeric neutral carbonyl complexes of transition metals. From its reaction with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ under controlled conditions, the organometallic compounds $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$, $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$, and $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$ can be obtained. (The latter complex can also be prepared by treating $[(\eta^5\text{-}C_5H_5)Cr(NO)(OCH_2CH_3)]_2$ in benzene with gaseous HCl.) In contrast, the analogous $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo or W) compounds react with ClNO in a 1:2 stoichiometry to produce $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ and $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ in comparable yields, but both of these products form intractable solids in the presence of an excess of ClNO. The cobalt complexes $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and $Co(CO)_3(NO)$ are both converted to $[Co(NO)_2Cl]_2$ by novel reactions with nitrosyl chloride, and (arene)$M(CO)_3$ (M = Mo or W) compounds form the polymeric $[M(NO)_2Cl_2]_n$ species via labile $M(CO)_2(NO)_2Cl_2$ intermediates under identical experimental conditions. Nitrosyl chloride apparently behaves as a nitrosonium salt in its reaction with $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ since the $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]^+$ cation is the principal product isolated, but it simply cleaves $Mn_2(CO)_{10}$ to yield the inert $Mn(CO)_5Cl$. Possible pathways leading to the formation of all products are presented.

Introduction

We recently reported[2] that the stoichiometric reaction of nitrosyl chloride with weakly nucleophilic metal carbonyl anions provides a convenient means of synthesizing neutral nitrosyl compounds such as $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ (M = Cr, Mo, or W), $W(CO)_4(NO)Cl$, $Mn(CO)_4(NO)$, and $Fe(CO)_2(NO)_2$ in reasonable yields. Further reactions between ClNO and the neutral carbonyl-containing compounds readily lead to neutral chloronitrosyl complexes in most instances. However, in some cases unexpected products result. For instance, when $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ is treated with ClNO, a minor product is $[(\eta^5\text{-}C_5H_5)Mo(NO)Cl_2]_2$, whose appearance, we believe,[2] reflects the fact that ClNO exists in solution as part of the equilibrium

$$2ClNO \rightleftharpoons 2NO + Cl_2$$

In other words, solutions of nitrosyl chloride may exhibit reactions that can be attributed to any of the chemical entities present in the above equilibrium. Even when nitrosyl chloride reacts as such with neutral carbonyl complexes, a number of different reaction modes can be envisaged for it. Among these are (1) displacement of ligands capable of donating a total of four electrons to a metal in a coordinatively saturated complex, (2) complete displacement of a hydrocarbon ligand regardless of the number of electrons that it formally donates to the metal, and (3) formal reaction as a nitrosonium salt with only NO^+ being coordinated to the metal center. This paper describes new reactions between ClNO and $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Cr, Mo, or W), $Co(CO)_3(NO)$, $(\eta^5\text{-}C_5H_5)Co(CO)_2$, (arene)$M(CO)_3$ (M = Mo or W), or $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, reactions which typify these reaction modes.

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to reported procedures, and their purity was ascertained by elemental analyses and/or melting point determinations. Melting points were taken in capillaries and are uncorrected. All solvents were dried by standard procedures (if necessary), distilled, and deaerated just prior to use, and all manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film. Proton magnetic resonance spectra were recorded on a Varian Associates T60 spectrometer with tetramethylsilane being employed as an internal standard. The low-resolution mass spectra were taken at 70 eV on an Atlas CH4B spectrometer using the direct-insertion method with the assistance of Dr. G. Eigendorf and Mr. G. Gunn. Elemental analyses were carried out by Mr. P. Borda of this department.

Reaction of Nitrosyl Chloride with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$. To a solution of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$[3] (2.0 g, 5.0 mmol) in dichloromethane (60 mL) at room temperature was added dropwise with rapid stirring a solution of ClNO[4] (2.5 g, 50 mmol) in dichloromethane (30 mL). Gas evolution occurred and the solution became yellow-green in color. The progress of the reaction was monitored by infrared spectroscopy, and the ClNO solution was added until the carbonyl absorptions due to the initial reactant had disappeared. The solvent was removed from the solution in vacuo, leaving a green residue. This residue was extracted with hexane to obtain an orange solution. The hexane was removed from the extracts under reduced pressure, and the resulting orange solid was sublimed at 40 °C (5×10^{-3} mm) onto a water-cooled probe. The orange sublimate (typically 0.70 g) was identified by its infrared spectrum as $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$.[5] The hexane-insoluble residue was dissolved in dichloromethane (25 mL). The addition of hexane (50 mL) to this solution precipitated a dark green solid which was collected by filtration. The filtrate was taken to dryness under reduced pressure, and the residue was redissolved in dichloromethane (10 mL). The resulting solution was filtered through a short (2×5 cm) Florisil column. The solvent was removed from the filtrate in vacuo to obtain ~0.80 g of a gold solid identified by its infrared spectrum as $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$.[5] The dark green solid collected previously was treated in the following manner. Volatile compounds were removed at 60 °C and 5×10^{-3} mm, and then the residue was dissolved in dichloromethane (30 mL). This solution was filtered and addition of hexane (60 mL) precipitated ~0.30 g of a dark green solid identified by its mass spectrum as $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$. The final filtrate contained a small amount (~0.1 g) of $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$ as evidenced by its infrared spectrum. However, this latter complex could not be satisfactorily purified because its solubility properties were identical with those exhibited by $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$. The yields of all product complexes depend markedly on the amount of nitrosyl chloride added.

Reaction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ with $Na(OCH_2CH_3)$. To a stirred solution of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$[5] (2.13 g, 10.0 mmol) in ethanol (120 mL) was added $Na(OCH_2CH_3)$ (0.80 g, 12.0 mmol) at room temperature. Immediately the reaction mixture became yellow-red and a fine white solid formed. The mixture was stirred for 1 h to ensure complete reaction. At the end of this time an infrared spectrum of the supernatant solution displayed strong absorptions at 1792 and 1685 cm^{-1} indicative of the $(\eta^5\text{-}C_5H_5)Cr(NO)_2(OCH_2CH_3)$ complex. The mixture was filtered, and removal of the solvent from the filtrate in vacuo yielded a red oil. During final drying at 25 °C (5×10^{-3} mm) for 1 h, the red oil transformed to a green solid. This solid was dissolved in dichloromethane and the resulting solution was filtered through a 3×8 cm Florisil column. The solvent was removed from the filtrate in vacuo to obtain olive green crystals (0.64 g, 33% yield) of analytically pure $[(\eta^5\text{-}C_5H_5)Cr(NO)(OCH_2CH_3)]_2$.

Anal. Calcd for $C_{14}H_{20}Cr_2N_2O_4$: C, 43.58; H, 5.21; N, 7.40. Found: C, 43.78; H, 5.26; N, 7.29. ν_{NO} (in CH_2Cl_2) 1660 cm^{-1}. Mp (under N_2) 233 °C dec.

Reaction of $[(\eta^5\text{-}C_5H_5)Cr(NO)(OCH_2CH_3)]_2$ with HCl(g). Dry HCl gas was bubbled through a solution of $[(\eta^5\text{-}C_5H_5)Cr(NO)(OCH_2CH_3)]_2$ (0.19 g, 0.50 mmol) in benzene (30 mL). The light green solution darkened in color, and HCl was added just until the reactant was completely consumed (as detected by infrared spectroscopy). The final reaction mixture was taken to dryness in vacuo, and the residue was crystallized from dichloromethane–hexane to obtain 0.16 g (92% yield) of pure $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$.

Anal. Calcd for $C_{10}H_{10}Cr_2N_2O_2Cl_2$: C, 32.90; H, 2.76; N, 7.67. Found: C, 32.50; H, 2.61; N, 7.66. ν_{NO} (in CH_2Cl_2) 1678 cm^{-1}. Mp (under N_2) 140 °C dec.

Reactions of $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$ and $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$ with NO. Both of these reactions were carried out in a similar manner. For example, $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$ (0.10 g, 0.29 mmol) was dissolved in dichloromethane (40 mL) and a stream of prepurified nitric oxide was bubbled through the solution. Immediately the green solution became green-brown, and the nitric oxide flow was stopped after several minutes. The solution was then filtered through a short (3×2 cm) Florisil column and the solvent was removed from the filtrate in vacuo to obtain a quantitative yield of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$. In the case of $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$, a much lower yield (~30%) of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ was obtained.

Reaction of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ with Cl_2. A saturated dichloromethane solution of Cl_2 was added dropwise at room temperature to a stirred orange solution of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$[5] (0.60 g, 3.0 mmol) in dichloromethane (30 mL). Gas was evolved and a green solid precipitated as the solution became yellow-green. Just enough chlorine was added to react with all of the $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$, as monitored by infrared spectroscopy. The final mixture was filtered and the solvent was removed from the filtrate in vacuo to obtain 0.26 g (41% yield based on Cr) of a green-gold solid which was identified by its infrared spectrum as $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$.

Reactions of $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo or W) with ClNO. To a stirred dichloromethane solution (50 mL) of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (0.74 g, 0.20 mmol) at room temperature was added dropwise a dichloromethane solution of ClNO. The reaction mixture became green-brown immediately and gas was evolved. Again, just enough nitrosyl chloride was added to react with all of the initial carbonyl dimer. The final solution was concentrated at reduced pressure to ~15 mL and was syringed onto a 2×20 cm Florisil column. The first band, orange, was collected and concentrated in vacuo to 10 mL. The addition of hexanes (30 mL) to this solution resulted in the crystallization of analytically pure $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$.

Anal. Calcd for $C_8H_5MoO_3Cl$: C, 34.25; H, 1.80. Found: C, 33.89; H, 1.93. ν_{CO} (in CH_2Cl_2) 2057, 1976 cm^{-1}.

Elution of the second band from the column produced a green solution which contained $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$, identified by its infrared spectrum.[2,5] This product was crystallized from the eluate by the addition of hexanes. The yields of both organometallic products were typically ~35% and were greatly dependent on the amount of ClNO added since both complexes reacted further with this reagent.

The reaction of $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ with nitrosyl chloride was identical in all aspects.

Reactions of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and $Co(CO)_3(NO)$ with ClNO. A solution of nitrosyl chloride in dichloromethane was added dropwise to a stirred solution of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (2 mL, 10 mmol) in CH_2Cl_2 (50 mL) cooled to −78 °C. Gas was evolved and the reaction was monitored by infrared spectroscopy. The addition of ClNO was stopped when the infrared bands due to the starting material had disappeared. The solvent was then removed in vacuo, leaving behind a black solid. This residue was sublimed at 90 °C (5×10^{-3} mm) onto a water-cooled probe to obtain 0.78 g (51% yield) of $[Co(NO)_2Cl]_2$.

Anal. Calcd for $Co_2N_4O_4Cl_2$: N, 18.14. Found: N, 17.78. ν_{NO} (in CH_2Cl_2) 1862, 1792 cm^{-1}.

The reaction of $Co(CO)_3(NO)$[6] with nitrosyl chloride was carried out in a similar manner. The product obtained in 58% yield was $[Co(NO)_2Cl]_2$ and it was isolated by sublimation as described above.

Reactions of $W(CO)_4(NO)X$ (X = Cl or Br) with Tetrahydrofuran. Both of these transformations were executed similarly. For example, a tetrahydrofuran solution (20 mL) containing $W(CO)_4(NO)Cl$[7] (0.50 g, 1.4 mmol) was stirred at room temperature until the infrared absorptions due to the initial reactant disappeared (~24 h). The solution was then taken to dryness in vacuo to obtain a quantitative yield of $[W(CO)_2(NO)(C_4H_8O)Cl]_2$.

Anal. Calcd for $W_2C_{12}H_{16}O_8N_2Cl_2$: C, 19.10; H, 2.12; N, 3.71; Cl, 9.39. Found: C, 19.20; H, 2.11; N, 3.56; Cl, 9.64. ν_{CO} (cm^{-1}) (in C_4H_8O) 2020, 1907; ν_{NO} (in C_4H_8O) 1636. Proton NMR, τ(in C_6D_6), (C_4H_8O) 5.60 (m), 7.85 (m).

The identical reaction between $W(CO)_4(NO)Br$ and tetrahydrofuran produced $[W(CO)_2(NO)(C_4H_8O)Br]_2$ (ν_{CO} (cm^{-1}) (in C_4H_8O) 2010, 1905; ν_{NO} (in C_4H_8O) 1635). These new complexes of tungsten are yellow-orange solids which are soluble in tetrahydrofuran, dichloromethane, and benzene to give solutions which decompose rapidly upon exposure to air. In the solid state the pure compounds are stable in air for at least 10 h, but they are best stored under nitrogen.

Reaction of (*o*-xylene)$Mo(CO)_3$ with ClNO. The compound (*o*-xylene)$Mo(CO)_3$[8] (0.74 g, 2.6 mmol) was dissolved in dichloromethane (40 mL) and the stirred solution was treated dropwise at room temperature with a solution of ClNO in the same solvent. Gas evolution was immediate, the yellow solution became orange-brown, and a green solid precipitated. Just enough ClNO was added to react completely with the initial carbonyl complex. After addition of the ClNO was completed, an infrared spectrum of the supernatant solution indicated the presence of a carbonylnitrosyl compound. However, continued stirring of the reaction mixture for several minutes caused more green solid to form. Hence, stirring was maintained until the supernatant liquid was colorless. The solvent was then removed in vacuo, and the green residue was dissolved in tetrahydrofuran to obtain a clear green solution. An infrared spectrum of this solution revealed that solvated $[Mo(NO)_2Cl_2]_n$[9] was the only nitrosyl complex present.

Reaction of $[Mo(NO)_2Cl_2]_n$ with $(C_6H_5)_3P$. The $[Mo(NO)_2Cl_2]_n$ produced in the previous reaction (0.59 g) was stirred in a refluxing benzene solution (60 mL) of $(C_6H_5)_3P$ (2.0 g, 7.6 mmol). After 1 h the initial mixture had become a clear green solution, thereby indicating that adduct formation was complete. The solvent was removed in vacuo and the yellow-green residue was extracted with dichloromethane (40 mL). Slow addition of hexanes (100 mL) to the extracts precipitated the well-known yellow-green solid $Mo(NO)_2Cl_2[(C_6H_5)_3P]_2$.[9]

Reactions of (arene)$W(CO)_3$ (arene = C_6H_6, $CH_3C_6H_5$, or $(CH_3)_3C_6H_3$) with ClNO. The reactions of nitrosyl chloride with (arene)$W(CO)_3$[10] complexes were carried out in a manner identical with that described previously for the molybdenum analogue. However, the progress of these reactions was slightly different. For example, when just enough ClNO to consume the tungsten reactant had been added, very little $[W(NO)_2Cl_2]_n$ had precipitated. An infrared spectrum of the reaction mixture revealed the presence of a carbonylnitrosyl complex which was not affected by the addition of an excess of nitrosyl chloride. This complex could be isolated by filtering the final reaction mixture and taking the filtrate to dryness in vacuo. The resulting red-brown solid was soluble in tetrahydrofuran, dichloromethane, and benzene, and slightly soluble in hexane. Pure samples of this compound could not be obtained because of its tendency to transform slowly to $[W(NO)_2Cl_2]_n$[9] in solution at room temperature. In fact, stirring a dichloromethane solution of this compound for 48 h quantitatively precipitated $[W(NO)_2Cl_2]_n$. The red-brown complex was tentatively formulated as $W(CO)_2(NO)_2Cl_2$ by virtue of its infrared spectrum (ν_{CO} (cm^{-1}) (in CH_2Cl_2) 2145, 2070; ν_{NO} (in CH_2Cl_2) 1815, 1725).

Reactions of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ with ClNO. To a stirred solution of $(\eta^5C_5H_5)Mn(CO)_3$ (0.40 g, 2.0 mmol) in dichloromethane (40 mL) at room temperature was added dropwise a solution of ClNO in dichloromethane. After a few minutes, gas was evolved and the solution became cloudy. The reaction was exothermic and a large amount of ClNO was consumed. When the initial complex had completely reacted (as indicated by infrared spectroscopy), the reaction mixture was taken to dryness in vacuo. The resulting residue was extracted with ethanol (95%) and the extracts were treated with a saturated aqueous solution of NH_4PF_6, thereby precipitating a bright yellow solid. This solid (0.38 g, 54% yield) was identified as $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]PF_6$ by its charactertistic infrared spectrum.[6]

The same mode of reaction occurred with $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$.

Reaction of $Mn_2(CO)_{10}$ with ClNO. A stirred dichloromethane solution (100 mL) of $Mn_2(CO)_{10}$ (1.0 g, 2.6 mmol) was treated at room temperature with an excess of ClNO. The yellow solution became orange initially, but no gas was evolved. The reaction mixture was stirred for 3 h, during which time a yellow solid precipitated and some gas evolution occurred. The solvent was then removed in vacuo, and the yellow residue was sublimed at 50 °C (5×10^{-3} mm) onto a water-cooled probe to obtain 0.23 g (38% yield) of $Mn(CO)_5Cl$.

Anal. Calcd for MnC_5O_5Cl: C, 26.06. Found: C, 25.99.

Results and Discussion

Reactions of Nitrosyl Chloride with $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Cr, Mo, or W) Complexes. The ability of nitrosyl chloride to react by various modes is clearly illustrated by its reaction with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$. If an excess of ClNO is employed, $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ is the major organometallic product obtained. However, if only sufficient ClNO to consume the original dimer is added, the principal organometallic products are $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ and $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$. Although both of these compounds are well known, their production in this reaction is somewhat unique. The formation of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ can be readily understood if one considers the initial species produced in this reaction. When only a small amount of nitrosyl chloride is reacted with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$, the presence of a carbonylnitrosyl complex is indicated by the infrared spectrum of the reaction mixture. This complex can be easily isolated and identified as $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. We have previously established[2,5] that this complex is smoothly converted to $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ by treatment with ClNO. The formation of the dicarbonylnitrosyl intermediate thus resembles the cleavage of the starting carbonyl dimer by nitric oxide[11] which also produces $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$. Therefore, the ultimate nitrosyl-containing product is probably formed by the following sequential reactions

$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 + 2ClNO \rightarrow 2(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO) + 2CO + Cl_2 \qquad (1)$$

$$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO) + ClNO \rightarrow (\eta^5\text{-}C_5H_5)Cr(NO)_2Cl + 2CO \qquad (2)$$

The other product, $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$, is rather unexpected. It is not produced in the reactions of Cl_2 with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$, $(\eta^5\text{-}C_5H_5)Cr(CO_2(NO)$, or $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ nor is it formed in reactions of the latter two compounds with nitrosyl chloride. It thus appears that a novel reaction mode of nitrosyl chloride with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ leads to this surprising product, i.e.

$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 \xrightarrow{ClNO} [(\eta^5\text{-}C_5H_5)CrCl_2]_2 \qquad (3)$$

This reaction parallels that described previously[12] for the carbonyl dimer with $CH_2{=}CHCH_2X$ (X = Br or I), i.e.

$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 \xrightarrow{CH_2=CHCH_2X} \text{“}(\eta^5\text{-}C_5H_5)CrX_2\text{”} \qquad (4)$$

in which carbonyl- or allyl-containing intermediates also were not observed.

The complex $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ has been well characterized,[13] and $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$ has been previously prepared by several other methods.[14] The latter compound has also been suggested[6] as an intermediate in the preparation of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ from $CrCl_3$, NaC_5H_5, and NO, although it was not isolated. A similar complex has been reported[15] to result from the reaction of chromocene with HCl(g). Most of these reports, however, are probably dealing with a solvated species such as $(\eta^5\text{-}C_5H_5)CrCl_2{\cdot}C_4H_8O$[12] since the preparative reactions are carried out in tetrahydrofuran. Desolvation of this species affords “$(\eta^5\text{-}C_5H_5)CrCl_2$”[12] as a blue-green amorphous powder which is not very soluble in common organic solvents. In contrast, the green $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$ that we isolate is very soluble, even in dichloromethane. Although the previously reported observations may pertain to various chloro complexes, the exact formulation of our compound is confirmed by its mass spectrum which is summarized in Table I. The spectrum exhibits the parent ion and the expected fragmentation pattern of the dimeric $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$, namely, the sequential loss of cyclopentadienyl and chlorine ligands. The molecular structure of this compound probably contains either two or four chlorine bridges between the metal atoms. When $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$ in dichloromethane is treated with nitric oxide, this dimeric structure is disrupted and $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ is produced. The yields of this latter conversion are quite low, and this may account for the low yields obtained in the original preparation of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$.[6]

A third, albeit minor, product of the reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ with ClNO is $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$. In view of the known reaction of Cl_2(g) with $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ to yield $[(\eta^5\text{-}C_5H_5)Mo(NO)Cl_2]_2$,[16] it is not

Table I. Low-Resolution Mass Spectral Data for $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$ and $[(\eta^5\text{-}C_5H_5)Cr(NO)L]_2$ (L = OCH_2CH_3 or Cl)[a]

$[(\eta^5\text{-}C_5H_5)CrCl_2]_2$			$[(\eta^5\text{-}C_5H_5)Cr(NO)(OEt)]_2$[b]			$[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$		
m/e	Rel abund	Assignment	*m/e*	Rel abund	Assignment	*m/e*	Rel abund	Assignment
374	5	$(C_5H_5)_2Cr_2Cl_4^+$	384	6	$(C_5H_5)_2Cr_2(OEt)_2(NO)_2^+$	364	4	$(C_5H_5)_2Cr_2Cl_2(NO)_2^+$
339	43	$(C_5H_5)_2Cr_2Cl_3^+$	354	68	$(C_5H_5)_2Cr_2(OEt)_2(NO)^+$	334	33	$(C_5H_5)_2Cr_2Cl_2(NO)^+$
304	5	$(C_5H_5)_2Cr_2Cl_2^+$	324	100	$(C_5H_5)_2Cr_2(OEt)_2^+$	304	34	$(C_5H_5)_2Cr_2Cl_2^+$
274	7	$C_5H_5Cr_2Cl_3^+$	295	15	$(C_5H_5)_2Cr_2(OEt)O^+$	182	100	$(C_5H_5)_2Cr^+$
187	7	$C_5H_5CrCl_2^+$	279	17	$(C_5H_5)_2Cr_2(OEt)^+$	152	29	$C_5H_5CrCl^+$
182	22	$(C_5H_5)_2Cr^+$	250	21	$(C_5H_5)_2Cr_2O^+$	117	31	$C_5H_5Cr^+$
152	100	$C_5H_5CrCl^+$	182	64	$(C_5H_5)_2Cr^+$	52	23	Cr^+
117	10	$C_5H_5Cr^+$	162	14	$C_5H_5CrOEt^+$			
65	16	$C_5H_5^+$	117	9	$C_5H_5Cr^+$			
52	20	Cr^+	52	14	Cr^+			

[a] The assignments involve the most abundant naturally occurring isotopes, i.e., ^{52}Cr and ^{35}Cl, in each fragment. [b] Et = CH_2CH_3.

unreasonable to expect that the analogous reaction between $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ and $Cl_2(g)$ could produce $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$. However, we find that this reaction results in an unusual disproportionation which leads to the formation of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ in high yields (with respect to the nitrosyl ligand). Furthermore, no reaction between $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ and Cl_2 or ClNO occurs in solution, thereby excluding these as pathways leading to the production of $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$. A fourth possibility might be the reaction of nitrosyl chloride with an intermediate carbonyl complex, but no absorptions attributable to carbonyl-containing species other than $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$ are observed in the infrared spectrum of the reaction mixture. Hence, we believe that $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$ is formed directly from $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ by the reaction

$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2 + 2ClNO \rightarrow [(\eta^5\text{-}C_5H_5)Cr(CO)(NO)Cl]_2 + 4CO \tag{5}$$

followed immediately by

$$[(\eta^5\text{-}C_5H_5)Cr(CO)(NO)Cl]_2 \rightarrow [(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2 + 2CO \tag{6}$$

as chlorine bridges are formed in the final product. The displacement of two carbonyl ligands by each ClNO added in reaction 5 represents a very common reaction mode of nitrosyl chloride and it has numerous precedents. For example, $[Re(CO)_4Cl]_2$ can be converted to $[Re(CO)_2(NO)Cl_2]_2$ by the process depicted in eq 7.[17] The spontaneous liberation of

$$[Re(CO)_4Cl]_2 + 2ClNO \rightarrow [Re(CO)_2(NO)Cl_2]_2 + 4CO \tag{7}$$

carbon monoxide invoked in reaction 6 appears to be a general property of a number of carbonylhalonitrosyl complexes, and some verified examples of such transformations are discussed in subsequent paragraphs.

The previously unknown dimeric complex $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$ can also be prepared by another method. When $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ is treated with $Na(OCH_2CH_3)$ or $Li(OCH_2CH_3)$ in tetrahydrofuran at room temperature, a metathetical reaction occurs and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(OCH_2CH_3)$ is formed as an unstable red oil. Upon exposure to high vacuum at room temperature the ethoxide derivative spontaneously loses nitric oxide to yield $[(\eta^5\text{-}C_5H_5)Cr(NO)(OCH_2CH_3)]_2$. This latter transformation can also be effected by eluting a dichloromethane solution of the ethoxodinitrosyl compound through an alumina column. Treatment of a benzene solution of the ethoxo dimer with HCl(g) affords $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$ quantitatively, i.e.

$$[(\eta^5\text{-}C_5H_5)Cr(NO)(OCH_2CH_3)]_2 + 2HCl \rightarrow [(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2 + 2CH_3CH_2OH \tag{8}$$

These chloro and ethoxo bimetallic compounds exhibit mass spectra (Table I) which are consistent with their formulation as dimers, and they exhibit a single absorption in their infrared spectra between 1660 and 1680 cm^{-1} attributable to the presence of a terminal nitrosyl group. Their molecular structures are presumably similar to those possessed by the complexes $[(\eta^5\text{-}C_5H_5)Cr(NO)L]_2$[18,19] (L = SCH_3, $S(C_6H_5)$, or $N(CH_3)_2$) in which L groups bridge two $(\eta^5\text{-}C_5H_5)Cr(NO)$ moieties. The chloro dimer is readily cleaved by nitric oxide, a quantitative conversion to $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ being observed.

In contrast to $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$, the analogous molybdenum and tungsten compounds $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo or W) react with an excess of nitrosyl chloride to produce intractable brown-black solids. However, if the progress of the reaction is monitored by infrared spectroscopy and the addition of ClNO is stopped at the appropriate time, the following reaction can be effected

$$[(\eta^5\text{-}C_5H_5)M(CO)_3]_2 + 2ClNO \rightarrow (\eta^5\text{-}C_5H_5)M(NO)_2Cl + (\eta^5\text{-}C_5H_5)M(CO)_3Cl + 3CO \tag{9}$$
$$M = Mo \text{ or } W$$

Unlike the chromium case, no carbonylnitrosyl intermediate which can account for the formation of the $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ complexes is observed during the course of this reaction. Thus, although we have established that the $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ complexes are conveniently produced by the reaction of ClNO and $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$,[2] these latter compounds are *not* detectable at any time during reaction 9. The derivation of the chlorodinitrosyl complexes from the parent dimers is therefore somewhat enigmatic.

The $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ (M = Mo or W) products may result from cleavage of the carbonyl dimers by ClNO in a manner similar to that described for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.[2] However, since a second complex is also formed in reaction 9, it is more probable that both $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ and $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ are produced from the same dimer molecule. Support for this inference comes from the fact that the infrared absorptions due to the two product complexes increase in intensity at similar rates as reaction 9 progresses and that both products are produced in comparable yields. Also, we have shown independently that the reaction between ClNO and $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ does not produce $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$. Hence, reaction 9 appears to follow a unique mechanistic pathway which involves ClNO and the dimers $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo or W). Since both $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ and $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ react further with ClNO, their yields from reaction 9 are drastically reduced if an excess of nitrosyl chloride is used.

Reactions of Nitrosyl Chloride with Other Neutral Carbonyl Complexes. Nitrosyl chloride reacts rapidly, even at −78 °C, with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ to give $[Co(NO)_2Cl]_2$ in moderate yields. Although the latter complex has been previously prepared by another route,[20] the fact that it is formed in this reaction reflects an unprecedented reaction mode of ClNO.

The displacement of olefinic ligands by nitrosyl chloride is not unknown,[21] but the displacement of the cyclopentadienyl ligand has not been previously reported. We also find that the same reaction mode occurs with $(\eta^5\text{-}C_5H_5)Re(CO)_3$ as the cyclopentadienyl ligand is again removed by ClNO to yield the known[17,22] $[Re(CO)_2(NO)Cl_2]_2$.

In quite similar reactions, (arene)$M(CO)_3$ (M = Mo or W) complexes react with nitrosyl chloride in dichloromethane at room temperature to eventually produce the polymeric $[M(NO)_2Cl_2]_n$ compounds. The arene ligand is apparently removed by ClNO in these conversions in a manner completely analogous to the displacement of the cyclopentadienyl group described above.[23] During the reactions involving the (arene)$W(CO)_3$ compounds, an intermediate carbonylnitrosyl complex is formed and this complex persists in solution for several hours at room temperature. We formulate this complex as $W(CO)_2(NO)_2Cl_2$ on the basis of the infrared spectrum which it exhibits in dichloromethane solution, namely, carbonyl-stretching absorptions at 2145 and 2070 cm^{-1} and nitrosyl-stretching absorptions at 1815 and 1725 cm^{-1}. Consistent with this formulation, these nitrosyl absorptions occur at higher frequencies than those reported for the related complexes $WL_2(NO)_2Cl_2$[9] (L = $(C_6H_5)_3P$, C_5H_5N, and $(C_6H_5)_3As$) since the carbonyl ligand is a better π acid. Dichloromethane solutions of $W(CO)_2(NO)_2Cl_2$ are red and air sensitive and slowly deposit $[W(NO)_2Cl_2]_n$ while being stirred at room temperature under an inert atmosphere. Hence, although $W(CO)_2(NO)_2Cl_2$ is stable in solution at ambient temperatures for short periods of time, the carbonyl ligands in the complex are quite labile and are eventually replaced by chlorine bridges in an associated complex as indicated in eq 10. During the reactions involving the (arene)$Mo(CO)_3$ compounds, the intermediate $Mo(CO)_2(NO)_2Cl_2$ species can be detected by infrared spectroscopy, but it is stable in solution for only a few minutes at room temperature. Like its tungsten analogue, $Mo(CO)_2(NO)_2Cl_2$ spontaneously evolves gas (cf. eq 10) and forms $[Mo(NO)_2Cl_2]_n$ which can be characterized as its triphenylphosphine adduct.[9]

$$nW(CO)_2(NO)_2Cl_2 \rightarrow [W(NO)_2Cl_2]_n + 2nCO \qquad (10)$$

This lability of carbonyl ligands appears to be an intrinsic property of transition metal carbonyl nitrosyl halides. For example, $W(CO)_4(NO)Cl$ readily evolves carbon monoxide when dissolved in tetrahydrofuran at room temperature and transforms to $[W(CO)_2(NO)(C_4H_8O)Cl]_2$, i.e.

$$2W(CO)_4(NO)Cl \xrightarrow{C_4H_8O} [W(CO)_2(NO)(C_4H_8O)Cl]_2 + 4CO \qquad (11)$$

The isolable product from this transformation is a yellow-orange solid to which we assign a dimeric formulation because of its diamagnetism. The molecular structure of this dimer in all likelihood contains two $W(CO)_2(NO)(C_4H_8O)$ groups linked by chlorine bridges so that the valence electron configuration of the metal satisfies the effective atomic number formalism.

Another transformation which follows a similar pattern is the formation of $[CO(NO)_2Cl]_2$ by the reaction of $Co(CO)_3(NO)$ with nitrosyl chloride. Although we could not detect an intermediate species in this instance, we believe that this conversion occurs via the sequential reactions 12 and 13, both of which are not without precedents. This propensity of carbonylhalonitrosyl complexes to lose carbonyl ligands and form dimeric or polymeric compounds by the concomitant formation of halide bridges can also be invoked to rationalize the products obtained from other reactions involving nitrosyl chloride and a neutral carbonyl complex. For example, $[M(CO)_4Cl_2]_2$ (M = Mo or W) complexes are converted by ClNO to $[M(NO)Cl_3]_n$ and small amounts of $[M(NO)_2Cl_2]_n$.[24] The trichloro polymer may well result from the reactions

$$Co(CO)_3(NO) + ClNO \rightarrow Co(CO)(NO)_2Cl + 2CO \qquad (12)$$

$$2Co(CO)(NO)_2Cl \rightarrow [Co(NO)_2Cl]_2 + 2CO \qquad (13)$$

$$[M(CO)_4Cl_2]_2 + 2ClNO \rightarrow [M(CO)_2(NO)Cl_3]_2 + 2CO \qquad (14)$$

$$(n/2)[M(CO)_2(NO)Cl_3]_2 \rightarrow [M(NO)Cl_3]_n + 2nCO \qquad (15)$$

which involve the same modes of transformation as reactions 12 and 13, respectively.

Finally, we have also studied the reactions of nitrosyl chloride with two types of manganese carbonyl complexes. Unlike its rhenium analogue, $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ reacts slowly at room temperature with ClNO and the cyclopentadienyl group is not displaced from the metal during the reaction. Instead, ClNO appears to behave analogously to a nitrosonium salt as the product obtained is the well-known cation $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]^+$[25] in yields comparable to those reported for previous preparations.[6] This cation does not react further even when treated with an excess of ClNO for several hours, thereby reflecting its inherent stability. The reaction of $Mn_2(CO)_{10}$ with nitrosyl chloride is also very slow at room temperature, and the only carbonyl product obtained is $Mn(CO)_5Cl$. No nitrosyl-containing species are detectable during the course of this reaction, and $Mn(CO)_5Cl$ does not react further with nitrosyl chloride.

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Registry No. $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$, 12194-12-6; ClNO, 2696-92-6; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, 12071-51-1; $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$, 12091-64-4; $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$, 12566-66-4; $(\eta^5\text{-}C_5H_5)Co(CO)_2$, 12078-25-0; $Co(CO)_3(NO)$, 14096-82-3; $W(CO)_4(NO)Cl$, 55057-86-8; $W(CO)_4(NO)Br$, 64044-38-8; (*o*-xylene)$Mo(CO)_3$, 12288-64-1; $(C_6H_6)W(CO)_3$, 12128-53-9; $(CH_3C_6H_5)W(CO)_3$, 12128-82-4; $((CH_3)_3C_6H_3)W(CO)_3$, 12129-69-0; $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, 12079-65-1; $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$, 12108-13-3; $Mn_2(CO)_{10}$, 10170-69-1; $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$, 12192-94-8; $[(\eta^5\text{-}C_5H_5)CrCl_2]_2$, 64024-36-8; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(OEt)$, 64024-35-7; $[(\eta^5\text{-}C_5H_5)Cr(NO)COEt)]_2$, 64024-34-6; $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$, 64024-33-5; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$, 12128-23-3; $(\eta^5\text{-}C_5H_5)Mo(NO)_2Cl$, 12305-00-9; $(\eta^5\text{-}C_5H_5)W(CO)_3Cl$, 12128-24-4; $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$, 53419-14-0; $[Co(NO)_2Cl]_2$, 13931-93-6; $[W(CO)_2(NO)(C_4H_8O)Cl]_2$, 64024-39-1; $[W(CO)_2(NO)(C_4H_8O)Br]_2$, 64024-38-0; $[Mo(NO)_2Cl_2]_n$, 30731-17-0; $Mo(NO)_2Cl_2[(C_6H_5)_3P]_2$, 14730-11-1; $W(CO)_2(NO)_2Cl_2$, 64024-37-9; $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]PF_6$, 31921-90-1; $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(NO)]PF_6$, 52202-14-9; $Mn(CO)_5Cl$, 14100-30-2.

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Reactions of Tetracyanoethylene Oxide with Some Noble Metal Complexes

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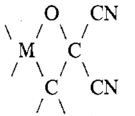
Reactions of tetracyanoethylene oxide with some noble metal complexes of platinum, palladium, rhodium, and iridium have been investigated, and a number of compounds have been isolated and characterized. The new complexes include both four-member metallocycles and the opened isomers, tricyanoethenolato complexes. The latter are formed via a thermal isomerization of the metallocycles. Photochemical isomerization of the metallocycles has also been observed and studied.

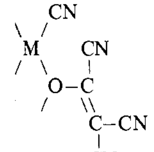
Introduction

Reactions involving the transformations of epoxides to various other organic compounds via catalysis by transition metal complexes have been described by a number of investigators.[2] These studies have dealt primarily with the organic products, with less attention having been given to organometallic intermediates that may have been formed. With a view toward isolating and characterizing organometallic intermediates, we have studied the reactions of 2,2,3,3-tetracyanooxacyclopropane (tetracyanoethylene oxide, TCNEO) with a number of noble metal complexes.

Previously we reported the preparation[3] of complexes of the type [PtL$_2$(TCNEO)] (L = tertiary phosphines and arsines) and the structure[4] of [Pt(AsPh$_3$)$_2$(TCNEO)]. We describe herein products of two types — cyclic complexes A and tricyanoethenolato complexes B—which have been obtained from reactions of TCNEO with low-valent transition metal complexes of rhodium, iridium, palladium, and platinum. Also described are the thermal and photochemical rearrangements of type A to type B complexes.



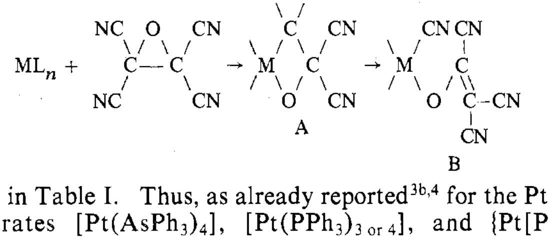
A



B

Results and Discussion

(1) Preparation of Complexes. Tetracyanoethylene oxide has been found to react readily with a number of low-valent noble metal substrates to give cyclic complexes (A) via insertion of the metallic moiety into the C–O bond, tricyanoethenolato complexes (B), presumably formed by subsequent isomerization of the initially formed cyclic complexes, or mixtures of A and B, eq 1. Data for the new complexes are given in Table I. Thus, as already reported[3b,4] for the Pt(0) substrates [Pt(AsPh$_3$)$_4$], [Pt(PPh$_3$)$_{3\text{ or }4}$], and {Pt[P(p-CH$_3$C$_6$H$_4$)$_3$]$_3$}, reactions occur immediately with TCNEO in benzene, THF, or CH$_2$Cl$_2$ at room temperature to give type A cyclic compounds (**1A**, **2A**, **3A** of Table II). Also, in the case of [Pt(CO)$_2$(PPh$_3$)$_2$], reaction with TCNEO in benzene at room temperature proceeds with gas evolution to give cyclic [Pt(PPh$_3$)$_2$(TCNEO)] (**2A**).



(1)

While most of the Pt(0) complexes which were studied gave metallocycles as described above, one compound gave a different product. From the reaction of [Pt(PPh$_2$Me)$_4$] and TCNEO in THF at room temperature, a compound believing to contain a tricyanoethenolato group, type B, was obtained, **4B**. Apparently the presence of more basic phosphines in the coordination sphere is conducive to the type A → type B transformation. In fact, it was found that type B complexes were obtained on workup of ligand-exchange reactions according to eq 2. Type A isomers are easily distinguished from the type B isomers by infrared spectroscopy. The latter complexes show several absorption bands (see Table II) in the range 2140–2220 cm^{-1} ascribable to cyano groups and an olefinic absorption at ca. 1590 cm^{-1}. In the type A cyclic compounds there is no olefinic band and there is only one C≡N stretching frequency at ca. 2220 cm^{-1}.

$$[\mathrm{PtL_2(TCNEO)}] \xrightarrow[-2\mathrm{L}]{+2\mathrm{L}'} \{\mathrm{PtL_2(CN)[-OC(CN){=}C(CN)_2]}\} \qquad (2)$$

1A, L = AsPh$_3$ **4B**, L′ = PPh$_2$Me
2A, L = PPh$_3$ **5B**, L′ = PEt$_3$

The palladium(0) complexes [Pd(PPh$_3$)$_4$] and {Pd[P(p-CH$_3$C$_6$H$_4$)$_3$]$_3$} reacted with TCNEO in THF at room temperature to give the type B complexes on workup, **7B** and **8B**. When the reaction was carried out at 0 °C, mixtures of type A and type B isomers were obtained. Attempts to isolate a pure type A isomer of palladium were not successful. The A → B rearrangement is very facile for palladium, but considerably more difficult for platinum, where in the case of cyclic [Pt(PPh$_3$)$_2$(TCNEO)] and the p-tolylphosphine analogue, temperatures of 170 and 140 °C, respectively, were required for the isomerization. Also, the isomerization was found to be sensitive to the nature of the solvent, going to completion only in protic solvents such as ethanol.

Reactions of TCNEO with complexes of nickel(0), rhodium(I), and iridium(I) did not always proceed as cleanly to give well-defined products as in the above-described reactions of palladium(0) and platinum(0) complexes.

When TCNEO and [Ir(PPh$_3$)$_2$(CO)Cl] were mixed in benzene at room temperature a darkening of the solution was