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Organometallic Nitrosyl Chemistry. 13.[1] Reactions of Sodium Dihydridobis(2-methoxyethoxy)aluminate with Some Cationic and Neutral Nitrosyl Complexes

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Sodium dihydridobis(2-methoxyethoxy)aluminate, I, undergoes metathetical reactions in benzene with equimolar amounts of the neutral iodonitrosyl complexes $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)(PPh_3)I$, $(\eta^5\text{-}C_5H_5)W(NO)I_2[P(OPh)_3]$, and $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$ to produce the new hydridonitrosyl species $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)(PPh_3)H$, $(\eta^5\text{-}C_5H_5)W(NO)(H)(I)[P(OPh)_3]$, and $[(\eta^5\text{-}C_5H_5)W(NO)(H)(I)]_2$, respectively. Treatment of $(\eta^5\text{-}C_5H_5)Cr(NO)_2X$ (X = NO_3, NO_2, I, $\eta^1\text{-}C_5H_5$, or BF_4), $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$, $(\eta^5\text{-}C_5H_5)Co(NO)I$, and $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$ with I in 1:1 stoichiometries affords the respective dimeric compounds $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$, $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$, and $[(\eta^5\text{-}C_5H_5)Mo(NO)I]_2$. These latter conversions probably proceed via thermally unstable hydrido complexes. The chromium dimer also results from the reaction of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(CO)]PF_6$ with the aluminum reagent and reacts further with I to produce in low yields a mixture of $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2)$, $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2$, and $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)(OH)$. In a similar manner, $Fe(NO)_3Cl$ is converted by I to $Fe_2(NO)_4(NH_2)_2$. The physical properties of all new complexes prepared are presented.

Introduction

We recently reported[2] the utility of $NaAlH_2(OCH_2CH_2OCH_3)_2$ (I) for the conversion of $(\eta^5\text{-}C_5H_5)M(NO)_2Cl$ (M = Cr, Mo, or W) complexes to either $(\eta^5\text{-}C_5H_5)M(NO)_2H$ (M = Mo or W) or $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$. This paper describes new reactions of this potent, yet selective, reductant with a variety of other organometallic nitrosyl complexes, reactions which demonstrate its ability to participate in metatheses or effect the reduction of a coordinated nitrosyl ligand.

Experimental Section

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commerical suppliers or prepared according to published procedures, and their purity was confirmed 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. Unless otherwise indicated, all manipulations were performed in an atmosphere of prepurified nitrogen.

Infrared (IR) spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601- or 2851-cm^{-1} band of polystyrene film. Proton magnetic resonance spectra were obtained on Varian Associates T60 or XL100 spectrometers with tetramethylsilane being employed as the standard. Mass spectra were recorded at 70 eV on an Atlas CH4B or AEI MS902 spectrometer by using the direct-insertion method with the assistance of Mr. J. W. Nip and Mr. G. Gunn. Elemental analyses were performed by Mr. P. Borda of this department.

Reaction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_3)$ with I. To a stirred green solution of $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_3)$[3] (0.66 g, 2.8 mmol) in benzene (30 mL) at room temperature was added dropwise a 0.5 M benzene solution of $NaAlH_2(OCH_2CH_2OCH_3)_2$ (I).[4] The solution gradually darkened and became purple. The progress of the reaction was monitored by IR spectroscopy, and the benzene solution of I was added until the nitrosyl absorptions due to the initial reactant had disappeared. Exactly 1 equiv of I was required for complete reaction. The final solution was concentrated in vacuo to ~5 mL and was transferred by syringe onto a 4 × 4 cm column of alumina (Woelm neutral, activity grade 1). Elution of the column with benzene developed a single red band which was collected and taken to dryness under reduced pressure to obtain red-purple, microcrystalline $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ (0.15 g, 31% yield), readily identifiable by its distinctive physical properties.[5]

Reactions of I with $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$,[6] $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$,[7] and $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$[7] in benzene, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]BF_4$[3] in CH_2Cl_2, and $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(CO)]PF_6$[8] in THF were carried out in a similar manner. In each instance, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ was the only nitrosyl-containing product formed.

Reaction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_3)$ with $NaBH_4$. To a stirred green solution of $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_3)$ (0.66 g, 2.8 mmol) in 1:1 benzene–tetrahydrofuran at room temperature was added an excess of solid $NaBH_4$ (0.20 g, 5.3 mmol). The reaction mixture began to darken after 1 h. IR monitoring indicated that the reaction was only partially completed after 24 h, and an additional 0.20 g of $NaBH_4$ was added. After an additional 24 h, the reaction was adjudged to be complete, and the reaction mixture was taken to dryness in vacuo. Purification of the residue by chromatography on alumina with benzene as eluant (vide supra) afforded 0.08 g (16% yield) of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$.

Reaction of $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$ with I. A stirred benzene solution (30 mL) containing $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$[9] (~2 mmol) was treated dropwise at room temperature with a benzene solution of I. The green-brown reaction mixture slowly became red-violet, and a solid precipitated. The reaction was monitored by IR spectroscopy, and the addition of the reducing agent was stopped when all the starting material had reacted. At this point, the mixture was concentrated under reduced pressure to ~10 mL and transferred by syringe to the top of a 2 × 5 cm column of alumina. Elution of the column with benzene produced a red-violet band which was collected and taken to dryness in vacuo. The resulting residue was identified as $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$[10] by its IR, NMR, and mass spectra.

Reaction of $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)(PPh_3)I$ with I. To a stirred benzene solution (40 mL) containing 2.0 g (3.6 mmol) of $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)(PPh_3)I$[9] at ambient temperature was added a benzene solution (1.0 mL) containing an equimolar amount of I. As the addition proceeded, the color of the former solution changed immediately from brown to red-brown, some gas evolution occurred, and a brown solid precipitated. Water (15 mL) was added to the final reaction mixture, and it was stirred for an additional 5 min. The benzene layer was then removed by syringe, and the remaining contents of the reaction flask were washed with benzene (6 × 20 mL). The benzene solutions were combined and were filtered through a 3.5 × 4 cm column of alumina (activity grade 1). The solvent was removed from the filtrate under reduced pressure to obtain a red oil.

Subsequent manipulations were performed in an argon atmosphere. The red oil was suspended in hexanes (60 mL), and the suspension was transferred onto a 2 × 8 cm column of alumina (activity grade

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4). Elution of the column with hexanes first developed a green band which was collected. Removal of solvent from the eluate afforded a small amount of a green solid which has yet to be identified and a large amount of triphenylphosphine. Continued elution with hexanes developed next a broad, orange band which required a 50:50 mixture of hexanes–benzene for complete removal from the column. The orange eluate was taken to dryness in vacuo to obtain 0.30 g (20% yield) of (η^5-$CH_3C_5H_4$)Mn(NO)(PPh_3)H as an orange, air-sensitive solid, mp (under N_2) 42.5 °C dec.

Anal. Calcd for $C_{24}H_{23}MnNOP$: C, 67.45; H, 5.42; N, 3.28. Found: C, 67.68; H, 5.57; N, 3.05. IR (C_6H_6): ν(NO) 1683 cm^{-1}. ^1H NMR (C_6D_6): δ 7.66–6.98 (15 H, m), 4.60 (1 H, s), 4.46 (1 H, s), 3.92 (2 H, s), 1.86 (3 H, s), –6.48 (1 H, d) [$^2J_{^1H-Mn-^{31}P}$ = 88.8 Hz].

Further elution of the column with benzene as eluant resulted in the development of a dark green band which was collected and taken to dryness under reduced pressure. The residue was recrystallized from CH_2Cl_2–hexanes to obtain air-stable, green microcrystals (0.016 g, 1% yield) of (η^5-$CH_3C_5H_4$)$_3Mn_3(NO)_4$ which was characterized by its elemental analysis, mass spectrum, and spectral properties.[11]

Reaction of (η^5-C_5H_5)Co(NO)I with I. To a toluene solution (80 mL) containing 0.43 g (1.5 mmol) of (η^5-C_5H_5)Co(NO)I[12] at –78 °C was added dropwise with stirring a benzene–toluene solution containing 1 equiv of I. The original green solution darkened, and then a tarry precipitate deposited as the addition proceeded. The final reaction mixture consisted of this precipitate and a virtually colorless supernatant liquid; it was permitted to warm slowly to room temperature. The solvent was removed under reduced pressure, the residue was extracted with tetrahydrofuran (3 × 25 mL), the extracts were filtered, and the filtrate was taken to dryness in vacuo.

The final residue was dissolved in 10 mL of CH_2Cl_2 and chromatographed on a 2 × 7 cm Florisil column with CH_2Cl_2 as eluant. A single, dark purple band developed and was collected, and the eluate was concentrated to 50 mL under reduced pressure. Addition of an equal volume of hexanes and slow concentration under reduced pressure induced the crystallization of [(η^5-C_5H_5)Co(NO)]$_2$[12] (0.12 g, 51% yield), whose identity was established by comparison with an authentic sample of the complex.

Reaction of (η^5-C_5H_5)W(NO)I_2[P(OPh)$_3$] with I. While a benzene suspension (40 mL) of (η^5-C_5H_5)W(NO)I_2[P(OPh)$_3$][1] (0.55 g, 0.65 mmol) was stirred at room temperature, a benzene solution containing 0.70 mmol of I was added dropwise. The original red solution became brown, and a brown solid precipitated. The final reaction mixture was treated with distilled H_2O (10 mL), the benzene layer was separated and filtered through a short (3 × 4 cm) column of anhydrous $MgSO_4$, and the filtrate was taken to dryness in vacuo. The resulting brown solid was dissolved in CH_2Cl_2 (~5 mL), and the solution was transferred to the top of a 2 × 8 cm Florisil column. Elution of the column with dichloromethane resulted in the development of a single yellow-orange band which was collected. Concentration of the eluate under reduced pressure to 25 mL, addition of hexanes (20 mL), and further concentration afforded orange crystals of analytically pure (η^5-C_5H_5)W(NO)(H)(I)[P(OPh)$_3$] (0.04 g, 9% yield), mp (under N_2) 112.0 °C dec. Anal. Calcd for $C_{23}H_{21}WNO_4PI$: C, 38.52; H, 2.95; N, 1.95. Found: C, 38.46; H, 2.93; N, 1.94. IR (CH_2Cl_2): ν(NO) 1642 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.33 (15 H, m), 5.32 (5 H, s), –1.98 (1 H, m) [$^2J_{^1H-W-^{31}P}$ = 111 Hz, $^1J_{^1H-^{183}W}$ = 54 Hz].

Reaction of [(η^5-C_5H_5)W(NO)I_2]$_2$ with I. Dropwise treatment of a stirred green-brown solution of [(η^5-C_5H_5)W(NO)I_2]$_2$[1] (1.00 g, 0.94 mmol) in benzene (60 mL) at room temperature by a benzene solution (8 mL) containing 0.94 mmol of I caused the solution to become dark green and a brown precipitate to form. Distilled water (40 mL) was added to the final reaction mixture, and the mixture was stirred for 15 min. The benzene layer was removed by syringe and was filtered through a 3 × 4 cm column of anhydrous $MgSO_4$. The dark green filtrate was taken to dryness in vacuo to obtain ~0.09 g of a bright green, thermally unstable solid. The solid was redissolved in 50 mL of benzene, an excess of neat P(OPh)$_3$ (0.27 mL, 0.33 g, 1.1 mmol) was added, and the mixture was stirred at ambient temperature for 20 min, whereupon it slowly darkened from green to brown. Solvent was removed under reduced pressure, and the resulting brown solid was purified by chromatography on Florisil with CH_2Cl_2 as eluant to obtain orange crystals (0.06 g, 9% yield) of (η^5-C_5H_5)W(NO)(H)(I)[P(OPh)$_3$] (vide supra).

Reaction of [(η^5-C_5H_5)Mo(NO)I_2]$_2$ with I. Solid [(η^5-C_5H_5)Mo(NO)I_2]$_2$[13] (1.93 g, 2.17 mmol) was suspended in benzene (200 mL) at room temperature, dissolving only slightly to give a pale violet solution. A 0.45 M benzene solution of I was added dropwise over a period of 1.5 h, the slow addition being required to permit the [(η^5-C_5H_5)Mo(NO)I_2]$_2$ to equilibrate with the solution. As I was added, a dark precipitate formed and the solution turned green; with stirring, it became orange; then as more starting material dissolved, the solution again became violet. The addition of I was stopped when the violet coloration no longer returned; 2 equiv of I was required to reach this point. The solvent was then removed in vacuo; the residue was dissolved in 15 mL of CH_2Cl_2; and the resulting dark solution was syringed onto a 3 × 8 cm alumina (activity grade 1) column. Elution with CH_2Cl_2 developed two bands: a leading pale green band which decomposed part way down the column and an orange band which required 300 mL of CH_2Cl_2 for complete elution. The eluate was taken to dryness under reduced pressure, and the residue was recrystallized from hot toluene to obtain 0.25 g (18% yield) of analytically pure, orange [(η^5-C_5H_5)Mo(NO)I]$_2$, mp (in air) 135 °C dec.

Anal. Calcd for $C_{10}H_{10}Mo_2N_2O_2I_2$: C, 18.89; H, 1.59; N, 4.41. Found: C, 19.14; H, 1.68; N, 4.47. IR (CH_2Cl_2): ν(NO) 1648 cm^{-1}.

The reaction between [(η^5-C_5H_5)Mo(NO)Cl_2]$_2$ and I in benzene was performed and worked up in an identical manner. No organometallic products were isolable by chromatography.

Reaction of [(η^5-C_5H_5)Cr(NO)$_2$]$_2$ with I. At room temperature 0.91 g (2.6 mmol) of [(η^5-C_5H_5)Cr(NO)$_2$]$_2$[5] was dissolved in benzene, and 2 equiv of I in benzene was added dropwise to the stirred solution. The red-purple solution gradually became orange-brown, and a small amount of a black precipitate deposited. After all the aluminum reagent had been added, the reaction mixture was stirred for an additional 0.5 h to ensure complete reaction. The mixture was then concentrated under reduced pressure to ~10 mL and was transferred onto a 3 × 8 cm Florisil column. Elution of the column with benzene developed two bands. The broad, dark green, first band eluted with ~250 mL of benzene. The solvent was removed from the eluate in vacuo, and the resulting residue was crystallized from dichloromethane–hexanes to obtain green crystals (0.129 g, 15% yield) of (η^5-C_5H_5)$_2Cr_2(NO)_3(NH_2)$[14] which was identified by its characteristic IR, NMR, and mass spectra.[11]

The orange second band was then eluted from the column with dichloromethane. Addition of hexanes to the eluate and slow concentration of the mixture under reduced pressure resulted in the formation of orange crystals (0.02 g, 2% yield) of (η^5-C_5H_5)$_2Cr_2(NO)_2(NH_2)_2$, mp (in air) 130 °C dec.

Anal. Calcd for $C_{10}H_{14}Cr_2N_4O_2$: C, 36.82; H, 4.33; N, 17.17. Found: C, 36.76; H, 4.20; N, 16.93. IR (THF): ν(NO) 1625 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.39 (5 H, s), 2.08 (2 H, br).

Finally, elution of the column with tetrahydrofuran produced a single brown-orange band which was collected and taken to dryness under reduced pressure. Crystallization of the residue from dichloromethane–hexanes afforded orange crystals (0.03 g, 3% yield) of (η^5-C_5H_5)$_2Cr_2(NO)_2(NH_2)(OH)$, mp (in air) 150 °C dec.

Anal. Calcd for $C_{10}H_{13}Cr_2N_3O_3$: C, 36.71; H, 4.00; N, 12.84. Found: C, 36.59; H, 3.83; N, 12.53, IR (THF): ν(NO) 1655, 1625 cm^{-1}. Mass spectrum: most intense parent ion m/z 326.9769.

Reaction of (η^5-C_5H_5)$_2$Cr$_2$(NO)$_3$(NH$_2$) with I. Two equivalents of I in benzene was added to a benzene solution (30 mL) containing 0.12 g (0.35 mmol) of the amide at room temperature. As the mixture was stirred, the initial green color changed to a dark orange-brown. IR monitoring of the reaction indicated that most of the reactant was consumed after 30 min. The final mixture was concentrated in vacuo and chromatographed on Florisil (vide supra) to obtain 0.035 g of unreacted (η^5-C_5H_5)$_2Cr_2(NO)_3(NH_2)$, 0.010 g of (η^5-C_5H_5)$_2Cr_2(NO)_2(NH_2)_2$, and ~0.001 g of (η^5-C_5H_5)$_2Cr_2(NO)_2(NH_2)(OH)$. The yields of the latter two complexes were 12% and 1%, respectively, on the basis of the amount of (η^5-C_5H_5)$_2Cr_2(NO)_3(NH_2)$ consumed.

Reaction of (η^5-C_5H_5)Cr(NO)$_2$Cl with NaNH$_2$. A THF solution (20 mL) containing 1.01 g (4.71 mmol) of (η^5-C_5H_5)Cr(NO)$_2$Cl[15] was added to an excess of solid $NaNH_2$ (0.65 g, 17 mmol), and the mixture was stirred at ambient temperature. Periodic monitoring of

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the supernatant liquid by IR spectroscopy showed a gradual disappearance of the absorptions due to the organometallic reactant as the solution changed from olive green to orange-brown and a black precipitate formed. After 1.5 h, the reaction mixture was filtered through a short (2 × 4 cm) column of Celite supported on a medium-porosity frit. The solvent was removed from the filtrate in vacuo, the residual solid was suspended in 10 mL of CH_2Cl_2, and the mixture was transferred to the top of a 2 × 6 cm Florisil column. Elution of the column with CH_2Cl_2 developed a single green band which was collected and taken to dryness. The golden solid thus obtained (~0.02 g) was identified as unreacted $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ by its IR and ^1H NMR spectra.[15]

Further elution of the column with THF resulted in the development of a dark orange-brown band which was collected. Removal of solvent from the eluate under reduced pressure followed by recrystallization of the residue from CH_2Cl_2–hexanes afforded 0.06 g (8% yield) of $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)(OH)$ which was identified by its characteristic spectral properties (vide supra).

Reaction of $Fe(NO)_3Cl$ with I. A stream of prepurified nitric oxide was passed over a vigorously stirred THF solution (100 mL) containing 1.0 g (3.3 mmol) of $[Fe(NO)_2Cl]_2$[16] for 20 min. The stirred solution was then placed under a nitrogen atmosphere, and a 0.5 M benzene solution of I was added dropwise. IR monitoring indicated that a slight excess of I was required to react completely with the $Fe(NO)_3Cl$ generated in situ, but the reaction mixture remained dark throughout. After the reaction was complete, the solvent was evaporated in vacuo; the residual solid was suspended in 10 mL of CH_2Cl_2; and the suspension was transferred onto a 3 × 8 cm Florisil column. A single brown band developed when the column was eluted with a 1:3 mixture of THF–CH_2Cl_2, and it was collected. The eluate was taken to dryness, and the remaining solid was crystallized by slow cooling of a concentrated 10:1 CH_2Cl_2–THF solution from room temperature to −20 °C to obtain 0.04 g (5% yield) of $Fe_2(NO)_4(NH_2)_2$, mp (under N_2) 176 °C dec.

Anal. Calcd for $H_4Fe_2N_6O_4$: C, 0.00; H, 1.53; N, 31.86. Found: C, 0.16; H, 1.52; N, 31.64. IR (CH_2Cl_2): ν(NO) 1763, 1727 cm^{-1}. ^1H NMR: ($CDCl_3$) δ 5.15 (br); ($(CD_3)_2CO$) δ 6.80 (br). Mass spectrum: most intense parent ion m/z 263.9013.

Reaction of $Fe(NO)_3Cl$ with $NaBH_4$. To a stirred solution (20 mL) containing 3.32 mmol of $Fe(NO)_3Cl$ (prepared in situ as described in the previous section) at room temperature was added solid $NaBH_4$ (0.25 g, 6.7 mmol). The reaction mixture immediately darkened, heat was given off, and gas evolution occurred. The final reaction mixture was worked up in a manner identical with that described in the preceding paragraph to obtain 0.03 g (7% yield) of $Fe_2(NO)_4(NH_2)_2$.

In a separate experiment, the $NaBH_4$ was added in small portions, and the IR spectrum of the supernatant liquid was recorded after each addition. The only detectable nitrosyl absorptions were those attributable to either the starting material or the isolated product.

Reaction of $Fe(NO)_3Cl$ with $NaNH_2$. $[Fe(NO)_2Cl]_2$ (0.62 g, 2.0 mmol) was dissolved in THF (30 mL) and converted to $Fe(NO)_3Cl$ as described above. Solid $NaNH_2$ (0.31 g, 8.0 mmol) was added, and the reaction mixture was stirred for 24 h at room temperature whereupon it gradually darkened. Filtration of the mixture, removal of solvent, and chromatography of the residue as before produced 0.054 g (10% yield) of $Fe_2(NO)_4(NH_2)_2$ which was identified by its distinctive physical properties (vide supra).

Results and Discussion

Reactions of Sodium Dihydridobis(2-methoxyethoxy)aluminate. (a) With Monomeric Chromium Nitrosyl Complexes. Previous work in this laboratory has established that reduction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (I) in toluene at room temperature produces $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ in 22% yield.[2] We believe that this reaction probably proceeds via the thermally unstable hydridochromium complex $(\eta^5\text{-}C_5H_5)Cr(NO)_2H$, which subsequently dimerizes to the observed product with concomitant expulsion of hydrogen.[17] Further support for the involvement of such a hydrido intermediate is provided by the present observation that $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ is formed in comparable yields during reactions of I with a variety of $(\eta^5\text{-}C_5H_5)Cr(NO)_2X$ precursors at ambient temperature, i.e.

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2X \xrightarrow[\text{benzene or } CH_2Cl_2]{I} [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 \quad (1)$$

$$X = NO_3,\ NO_2,\ I,\ \eta^1\text{-}C_5H_5,\ \text{or } BF_4$$

Monitoring of the progress of reaction 1 by infrared spectroscopy indicates that the optimum stoichiometric ratio of reactants is 1:1 and that the dimeric species is the only nitrosyl-containing product formed. These reactions also demonstrate the ability of I to substitute H^- for both halide and pseudohalide ligands and to transfer H^- to a coordinatively unsaturated metal center such as that in $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]BF_4$.

Conversion 1 can also be effected in tetrahydrofuran with $NaBH_4$ being employed in place of I, but the yield of the dimeric product is lower. For instance, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ is isolable in only 15% yield from such a reaction when $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_3)$ is used as the starting material. A similar observation has been reported for the reduction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ by either I or $NaBH_4$.[2]

The ubiquitous nitrosyl dimer also results from reaction 2,

$$[(\eta^5\text{-}C_5H_5)Cr(NO)_2(CO)]PF_6 \xrightarrow[\text{THF}]{I} [(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 \quad (2)$$

a transformation which parallels the synthesis of $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$[10] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$[18] by hydride attack on the isoelectronic cations $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]^+$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$, respectively. Presumably, reaction 2 again occurs via the unstable $(\eta^5\text{-}C_5H_5)Cr(NO)_2H$ since it is known that treatment of the analogous cation $[(\eta^5\text{-}C_5H_5)W(NO)_2(CO)]^+$ with $NaBH_4$ produces the thermally stable complex $(\eta^5\text{-}C_5H_5)W(NO)_2H$.[2] From a synthetic viewpoint, however, reactions 1 and 2 are not particularly useful since $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ is best prepared by the reaction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ with sodium amalgam in benzene.[5]

(b) With Some Monomeric Iodonitrosyl Complexes. Just as with $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$ (eq 1), I also undergoes simple metathetical reactions with other monomeric iodonitrosyl complexes to produce hydridonitrosyl species which may or may not be thermally stable at ambient temperature. Examples of these reactions are summarized in eq 3–5. Again, the

$$(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I \xrightarrow[\text{benzene}]{I} [(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2 \quad (3)$$

$$(\eta^5\text{-}CH_3C_5H_4)Mn(NO)(PPh_3)I \xrightarrow[\text{benzene}]{I} (\eta^5\text{-}CH_3C_5H_4)Mn(NO)(PPh_3)H \quad (4)$$

$$(\eta^5\text{-}C_5H_5)Co(NO)I \xrightarrow[\text{toluene, } -78\ °C]{I} [(\eta^5\text{-}C_5H_5)Co(NO)]_2 \quad (5)$$

optimum stoichiometry of the reactants is 1:1, and the transformations proceed smoothly and in reasonable yields. Due to the thermal instability of $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$,[9] a precise yield for reaction 3 could not be determined. Nevertheless, an overall yield of ~65% could be achieved for the conversion of the manganese dimer to the iodide by the action of I_2 followed by reduction with I back to the dimer.

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[15] Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126–31.

[16] Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1975**, *14*, 1875–8.

[17] Cf. the thermal dimerization of $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ described in ref 6.

[18] Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3172–7.

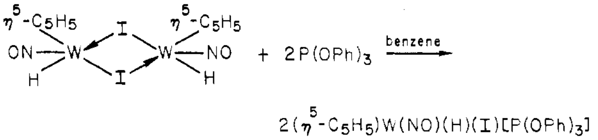
The dimeric products formed in reactions 3 and 5 again probably arise from the thermal decomposition of the corresponding monomeric hydridonitrosyl complexes, but we have been unable to obtain any direct physical evidence for the existence of these species. However, consistent with the view that (η^5-C_5H_5)Mn(CO)(NO)H is the labile intermediate in reaction 3 is the fact that (η^5-$CH_3C_5H_4$)Mn(NO)(PPh_3)H can be isolated from reaction 4. Evidently, introduction of the better electron-donating $CH_3C_5H_4$ and PPh_3 groups into the coordination sphere of the manganese atom stabilizes the latter hydride, whereas the analogous hydridocarbonyl complex in reaction 3 is so unstable that it cannot be detected by conventional spectroscopic techniques.

Since reaction 4 represents the first preparation of (η^5-$CH_3C_5H_4$)Mn(NO)(PPh_3)H, the physical properties of this complex merit delineation. It is an orange, air-sensitive solid (mp 42.5 °C dec), which is freely soluble in benzene, is sparingly soluble in hexanes, and reacts with CH_2Cl_2. The ^{1}H NMR spectrum of the compound in C_6D_6 exhibits resonances assignable to the PPh_3 [δ 7.66–6.98 (15 H, m)], η^5-$CH_3C_5H_4$ [δ 4.60 (1 H, s), 4.46 (1 H, s), 3.92 (2 H, s), 1.86 (3 H, s)], and H [δ −6.48 (1 H, d), $^2J_{^1H-Mn-^{31}P} = 88.8$ Hz] ligands. Its IR spectrum in benzene displays a strong absorption at 1683 cm^{-1} attributable to a terminal nitrosyl group. However, the complex decomposes slowly both in solution and in the solid state when maintained in an atmosphere of prepurified argon. For instance, a red benzene solution of (η^5-$CH_3C_5H_4$)Mn(NO)(PPh_3)H at room temperature slowly becomes dark green and deposits a brown solid. Monitoring of this transformation by ^{1}H NMR spectroscopy reveals a gradual diminution of the resonances due to the hydrido complex and a concomitant increase in intensity of two sharp signals at δ 1.64 and 4.60 of relative intensity 3:4 due to the well-known, green trimetallic complex (η^5-$CH_3C_5H_4$)$_3$Mn$_3$(NO)$_4$.[11] The transformation is complete after 48 h. Consequently, purification of the hydrido product of reaction 4 by column chromatography also affords trace amounts of the trimetallic species. The fact that (η^5-$CH_3C_5H_4$)Mn(NO)(PPh_3)H decomposes thermally in this manner rather than to [(η^5-$CH_3C_5H_4$)Mn(NO)(PPh_3)]$_2$ is presumably a reflection of the considerable lability of the PPh_3 group.

(c) With [(η^5-C_5H_5)M(NO)X_2]$_2$ (M = Mo, X = Cl, I; M = W, X = I) Complexes. In view of the reactivity patterns of I described above, it was of interest to investigate its reactions with complexes containing both bridging and terminal halide ligands. It seemed reasonable that selective substitution of the terminal halides could be achieved while leaving the halide bridges intact. Indeed, just such a transformation does occur when [(η^5-C_5H_5)W(NO)I_2]$_2$ is treated with 1 equiv of I at room temperature; e.g., see eq 6. The unprecedented product of reaction 6 is a bright green, air-sensitive solid which is soluble in most common organic solvents except paraffin hydrocarbons. However, the compound is thermally unstable both in solution (benzene > CH_2Cl_2 > THF in order of decreasing stability) and in the solid state (half-life of ~24 h), decomposing to a brown, intractable solid. Consequently, analytically pure samples of this compound could not be obtained. Nevertheless, its physical properties are consistent with it having the molecular structure shown in eq 6. Its IR spectrum (in CH_2Cl_2) displays a strong nitrosyl absorption at 1640 cm^{-1}, and its ^{1}H NMR spectrum (in $CDCl_3$) consists of two singlets at δ 5.32 and −1.22 of relative intensity 5:1 assignable to the cyclopentadienyl protons and hydrides, respectively, although ^{183}W–^{1}H coupling is not observed. The dimeric nature of the complex is confirmed by its mass spectrum (at a probe temperature of 130 °C) which exhibits peaks attributable to the parent ion and ions corresponding to the sequential loss of ligands. Unfortunately, overlapping of some medium to strong intensity peaks in the lower mass range makes unambiguous assignments difficult, especially in the light of the polyisotopic nature of tungsten.

(6)

The dimeric product of reaction 6 can also be characterized chemically since it readily reacts with triphenyl phosphite to produce a new tungsten hydridonitrosyl complex (see eq 7).



(7)

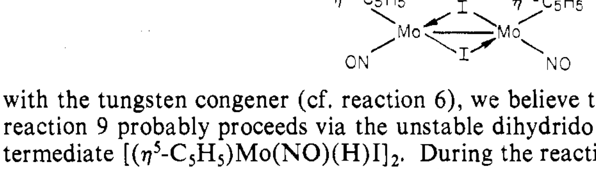
The same product can also be obtained in 9% yield by treatment of the appropriate iodo precursor with I in a 1:1 mole ratio (see eq 8). The hydride product is an orange, diamagnetic solid which can be handled in air for short periods of time without the occurrence of noticeable decomposition.

$$(\eta^5\text{-}C_5H_5)W(NO)I_2[P(OPh)_3] \xrightarrow[\text{benzene}]{\text{I}} (\eta^5\text{-}C_5H_5)W(NO)(H)(I)[P(OPh)_3] \quad (8)$$

It is quite soluble in polar organic solvents, but only sparingly soluble in nonpolar ones, to give air-sensitive orange solutions. Its spectral properties confirm the monomeric nature of the complex and the presence of a W–H bond. Thus, its mass spectrum (at a probe temperature of 150 °C) displays peaks corresponding to the parent ion P$^+$, (P − I)$^+$, and (P − P(OPh)$_3$)$^+$, and its ^{1}H NMR spectrum (in $CDCl_3$) exhibits resonances due to the hydride centered at δ −1.98 which reflect coupling to both the W and P atoms ($^1J_{^1H-^{183}W} = 54$ Hz and $^2J_{^1H-W-^{31}P} = 111$ Hz). These coupling constants are of the same order of magnitude as those reported for analogous hydridocarbonyl complexes,[19] but the hydride resonance occurs at slightly higher field than that observed for (η^5-C_5H_5)W(NO)$_2$H[2] (δ 2.06) under identical conditions.

It appears that reactions 7 and 8 represent generally applicable methods for the synthesis of a series of complexes of the type (η^5-C_5H_5)W(NO)(H)(I)(L), where L is any ligand capable of donating two electrons to the metal center. Work is presently under way to prepare other members of this series in order to determine the effect of various ligands on the physical and chemical properties of hydridonitrosyl complexes of tungsten. Such a study is of interest in light of the surprising hydridic character of (η^5-C_5H_5)W(NO)$_2$H.[2]

When [(η^5-C_5H_5)Mo(NO)I_2]$_2$ is treated with 1 equiv of I at room temperature, the well-known dimer [(η^5-C_5H_5)Mo(NO)I]$_2$[20] is formed in 6% yield. The yield can be improved to 18% when 2 equiv of I is employed (see eq 9). By analogy with the tungsten congener (cf. reaction 6), we believe that reaction 9 probably proceeds via the unstable dihydrido intermediate [(η^5-C_5H_5)Mo(NO)(H)I]$_2$. During the reaction, a green color, perhaps due to the intermediate, appears after the addition of each aliquot of I; but this color persists only for several seconds before being replaced by the characteristic



(9)

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(19) See for example: Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231–81 and references cited therein.

(20) James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1971**, 1068–73.

Table I. Low-Resolution Mass Spectral Data for $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)X$ ($X = NH_2$ or OH) Complexes[a]

$X = NH_2$			$X = OH$		
m/z	rel abund	assignt	m/z	rel abund	assignt
326	39	$(C_6H_5)_2Cr_2(NO)_2(NH_2)_2^+$	327	25	$(C_5H_5)_2Cr_2(NO)_2(NH_2)(OH)^+$
296	60	$(C_5H_5)_2Cr_2(NO)(NH_2)_2^+$	297	81	$(C_5H_5)_2Cr_2(NO)(NH_2)(OH)^+$
266	100	$(C_5H_5)_2Cr_2(NH_2)_2^+$	280	11	$(C_5H_5)_2Cr_2(NO)O^+$
249	11	$(C_5H_5)_2Cr_2(NH)^+$	267	65	$(C_5H_5)_2Cr_2(NH_2)(OH)^+$
200	17	$(C_5H_5)Cr_2(NH_2)(NH)^+$	250	100	$(C_5H_5)_2Cr_2O^+$
182	70	$(C_5H_5)_2Cr^+$	201	11	$(C_5H_5)Cr_2(NH_2)O^+$
148	5	$(C_5H_5)_2Cr_2(NO)(NH_2)_2^{2+}$	182	79	$(C_5H_5)_2Cr^+$
133	36	$(C_5H_5)Cr(NH_2)^+$	133.5	21	$(C_5H_5)_2Cr_2(NH_2)(OH)^{2+}$
117	21	$C_5H_5Cr^+$	117	19	$C_5H_5Cr^+$
52	19	Cr^+	52	25	Cr^+

[a] The assignments involve the most abundant naturally occurring isotopes in each fragment.

orange color of the final product. The species responsible for the green color cannot be detected by IR spectroscopy. Curiously, thermal decomposition of $[(\eta^5\text{-}C_5H_5)W(NO)(H)I]_2$ either in the solid state or in solution does not result in the formation of the analogous $[(\eta^5\text{-}C_5H_5)W(NO)I]_2$ (vide supra), a complex which has yet to be prepared.

In view of reaction 9, it was hoped that the reaction between $[(\eta^5\text{-}C_5H_5)Mo(NO)Cl_2]_2$ and I would afford the still unknown $[(\eta^5\text{-}C_5H_5)Mo(NO)Cl]_2$ complex in a similar manner. While the two reagents do react, no organometallic products can be isolated from the final reaction mixture. Previously attempted reductions of $[(\eta^5\text{-}C_5H_5)Mo(NO)Cl_2]_2$ with sodium amalgam, zinc dust, or $NaBH_4$ have also been unsuccessful.[21] These failures may reflect the inability of the Cl atoms to bridge the Mo centers in the desired product.

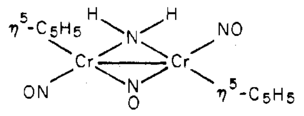
(d) With $[(\eta^5\text{-}C_5H_5)Cr(NO_2]_2$. The 1:1 stoichiometry of the reactants in reactions 1 and 2 is important for the formation of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ in maximum yields since the dimeric product can react further with the reducing agent. Hence, we have found that 2 equiv of I is required to consume completely $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and produce, albeit in low yields, a mixture of $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2)$, $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2$, and $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)(OH)$. The latter products appear to be formed by the sequential reactions (10) and (11) since a slight excess of I in reactions 1 and 2

$$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2 \xrightarrow[\text{benzene}]{\text{I}} (\eta^5\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2) \tag{10}$$

$$(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2) \xrightarrow[\text{benzene}]{\text{I}} (\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2 + (\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)(OH) \tag{11}$$

produces just a trace of $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2)$, and reaction 11 can be performed independently. The products of reaction 11 do not react further with I under ambient conditions.

The complex $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2)$ was first isolated in 1% yield from the reduction of $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ with $NaBH_4$ in water–benzene,[14] and it has recently been obtained as a byproduct of the reactions of carbanions with $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$.[22] It has been completely characterized and is known to possess the molecular structure I in the solid state.[23]



I

In terms of their gross stereochemical features, the two new complexes formed in reaction 11 are probably isostructural with the monoamido complex, with the bridging NO group in the latter being replaced by either an NH_2 or an OH group in the former species.

The diamido complex, $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2$, is an air-stable, nonvolatile, orange solid which begins to decompose gradually at 130 °C. It has limited solubility in benzene, dichloromethane, and tetrahydrofuran; but the orange solutions formed are air and water stable. An IR spectrum of a THF solution of the complex exhibits a strong absorption at 1625 cm^{-1} attributable to the terminal nitrosyl ligands. The weak $\nu(NH)$ absorptions at 3380 and 3330 cm^{-1} can only be observed in the IR spectrum of the complex in a concentrated Nujol mull, but they occur in the same range as those reported for $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2)$.[14] The low-resolution mass spectrum of the complex (taken with a probe temperature of 220 °C and summarized in Table I) is consistent with its formulation as a dimer and displays a fragmentation pattern similar to that observed for $[(\eta^5\text{-}C_5H_5)Cr(NO)Cl]_2$.[24] For example, peaks due to metastable ions can be detected at $M^* = 239$ and 125, and they are assignable to the fragmentation processes $(C_5H_5)_2Cr_2(NO)(NH_2)_2^+ \rightarrow (C_5H_5)_2Cr_2(NH_2)_2^+$ and $(C_5H_5)_2Cr_2(NH_2)_2^+ \rightarrow (C_5H_5)_2Cr^+$, respectively. However, peaks corresponding to bimetallic ions are relatively more abundant in the mass spectrum of the diamido species. The ^1H NMR spectrum of the compound in $CDCl_3$ consists of a sharp resonance at δ 5.39 and a broad resonance at δ 2.08 of relative intensity 5:2 which are attributable to the cyclopentadienyl and amido protons, respectively. Since cis–trans interconversions of the related $[(\eta^5\text{-}C_5H_5)Cr(NO)(NMe_2)]_2$ complex are known to begin only at elevated temperatures,[25] this spectrum probably indicates that only one isomer (either cis or trans) of $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2$ exists in solution at ambient temperatures. Isomerization could not be induced to occur by heating a solid sample of the complex at 125 °C for 1.5 h.

The physical properties of the other new dichromium complex isolated generally resemble those displayed by the diamido compound. Thus, $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)(OH)$ is an orange-brown solid which can be handled in air for short periods of time. It is moderately soluble in benzene, CH_2Cl_2, and THF to yield air-sensitive solutions. Its IR spectra display characteristic strong $\nu(NO)$ (1655 and 1625 cm^{-1} in THF) and weak ν(NH or OH) absorptions (3490, 3405, and 3320 cm^{-1} in a Nujol mull); and its mass spectrum (Table I, probe temperature of 200 °C) confirms its bimetallic nature.[26]

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(21) McCleverty, J. A.; Seddon, D. *J. Chem. Soc., Dalton Trans.* **1972**, 2526–30.

(22) Müller, J.; Schmitt, S. *J. Organomet. Chem.* **1978**, *160*, 109–14.

(23) Chan, L. Y. Y.; Einstein, F. W. B. *Acta Crystallogr., Sect. B* **1970**, *26*, 1899–905.

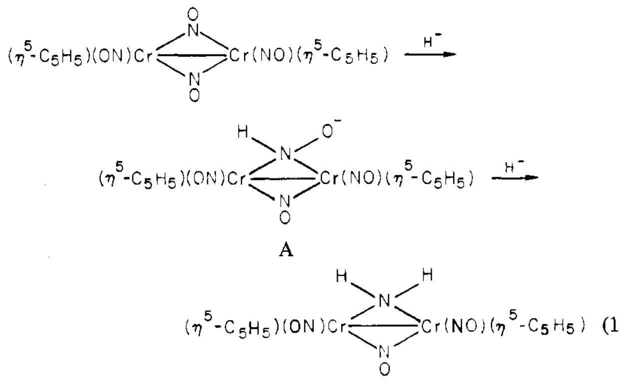
(24) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1977**, *16*, 3173–8.

(25) Ahmad, M.; Bruce, R.; Knox, G. *Z. Naturforsch., B* **1966**, *21*, 289.

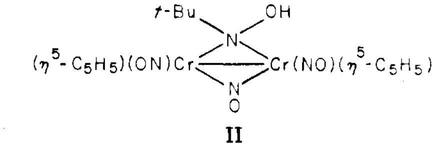
(26) The identity of the hydroxo complex was also confirmed by high-resolution mass spectrometry: calcd for $C_{10}H_{13}N_3O_3{}^{52}Cr^{53}Cr$ m/z 327.9768, found m/z 327.9769; calcd for $C_{10}H_{13}N_3O_3{}^{52}Cr_2$ m/z 326.9767, found m/z 326.9769; calcd for $C_{10}H_{13}N_2O_2{}^{52}Cr_2$ m/z 296.9787, found m/z 296.9789.

Interestingly, the mass spectrum also exhibits a metastable peak at M* = 234 indicative of the fragmentation process $(C_5H_5)_2Cr_2(NH_2)(OH)^+ \rightarrow (C_5H_5)_2Cr_2O^+$. A similar loss of NH_3 occurs during the fragmentation of the diamido complex (Table I). However, unlike for $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2$, the ^1H NMR spectrum of the hydroxo compound in $CDCl_3$ consists of three sharp resonances at δ 5.29, 5.48, and 5.55 due to the cyclopentadienyl protons in addition to two weak, broad signals at δ 2.62 and 3.42 attributable to NH_2 and/or OH protons. Apparently, the complex exists in solution as a mixture of isomers, these being presumably the one trans and two cis geometrical isomers expected if its molecular structure resembles that of $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2)$ (vide supra). These isomers do not readily interconvert in solution at ambient temperature since they can be partially separated by fractional crystallization from CH_2Cl_2–hexanes, and the ^1H NMR spectra of the crystallized materials in $CDCl_3$ display differing intensity ratios of the three C_5H_5 resonances. The solubility differences of the isomers are not sufficiently large, however, to allow the isolation of any one isomer in this manner. Nevertheless, satisfactory elemental analyses can be obtained for any of the crystalline species produced.

The formation of the amido products in reactions 10 and 11 can be viewed as arising from the nucleophilic attack of H^- on the nitrogen atom of a bridging nitrosyl ligand. The monoamido complex could thus result from the two-step mechanism (12) with the O^{2-} released being scavenged by the Lewis acid present in the reaction mixture. A similar sequence of reactions involving the monoamido species as the initial reactant would then afford the diamido compound. The fact that the complex II can be prepared by the reaction of *t*-BuLi with $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and subsequent hydrolysis[22] provides supporting evidence for the involvement of an intermediate such as A which itself may be stabilized by a coordinate O→Al bond involving the bridging HNO group. However, this rationale is contrary to the expectation that the N atoms of terminal NO groups should be attacked preferentially by nucleophiles;[27] and so it is possible that the isolated products are simply the most thermodynamically stable species resulting from rearrangements of precursors formed by the reduction of terminal NO ligands in the initial reactant. In this connection, though, it can be noted that the terminal nitrosyl groups of $[(\eta^5\text{-}C_5H_5)Cr(NO)(NH_2)]_2$ undergo no reaction with I under ambient conditions. Nevertheless, the reactivity of these organometallic nitrosyl complexes toward H^- contrasts with that reported for $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$ and $(\eta^5\text{-}C_5H_5)$-Ni(NO).[28] Both of the latter species are converted to nitrosyl-free cyclopentadienylhydrido clusters when treated with $LiAlH_4/AlCl_3$ in THF at 20 °C and then hydrolyzed.



(12)



II

The origins of the hydroxo complex, $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)(OH)$, are somewhat perplexing at the present time since several possible oxygen sources are present in the reaction mixture. It is intriguing, nonetheless, that it is the only nitrosyl-containing product formed when $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$ is treated with $NaNH_2$ in THF at room temperature.

(e) With $Fe(NO)_3Cl$. In view of the reactions of I with monomeric iodonitrosyl complexes of first-row transition metals described in section b, it was hoped that treatment of $Fe(NO)_3Cl$ with a hydridic reagent would produce the as yet unknown binary nitrosyl $Fe_2(NO)_6$ in an analogous manner. However, when either I or $NaBH_4$ is used as the reductant in reaction 13, the only nitrosyl product isolable in low yields

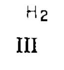
$$Fe(NO)_3Cl \xrightarrow[\text{benzene and/or THF}]{\text{I or NaBH}_4} Fe_2(NO)_4(NH_2)_2 \quad (13)$$

is $Fe_2(NO)_4(NH_2)_2$, a species which could be formed via further reduction of initially produced $Fe_2(NO)_6$ in much the same way that $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2$ is formed from $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_4$ (section d). $Fe_2(NO)_4(NH_2)_2$ can also be synthesized by reaction 14, an observation which indicates

$$Fe(NO)_3Cl \xrightarrow[\text{THF}]{\text{NaNH}_2} {}^1/_2[Fe(NO)_2(NH_2)]_2 \quad (14)$$

the thermodynamic stability of the dimer and suggests that in reaction 13 it could also result from the association of monomeric species formed by initial reduction of $Fe(NO)_3Cl$.

$Fe_2(NO)_4(NH_2)_2$ is a golden-brown, air- and water-stable solid which is sparingly soluble in most common organic solvents. Its molecular structure is probably similar to that found for other $[Fe(NO)_2X]_2$ (X = I, SEt, or $P(CF_3)_2$) complexes,[29] namely, structure III, in which the local geometry



III

about the Fe atoms is approximately tetrahedral. Thus, the IR spectrum of the complex in CH_2Cl_2 exhibits strong ν(NO) absorptions at 1763 and 1727 cm^{-1}; and its ^1H NMR spectra display a broad resonance (δ 5.15 in $CDCl_3$; δ 6.80 in $(CD_3)_2CO$) due to the amido protons. Its mass spectrum (recorded with a probe temperature of 80 °C and summarized in Table II) indicates that the terminal nitrosyl ligands are lost preferentially from the dimer during the fragmentation

Table II. High-Resolution Mass Spectral Data for $Fe_2(NO)_4(NH_2)_2$

m/z calcd	*m/z* measd	rel abund	assignt[a]
263.8992	263.9013	70	$Fe_2(NO)_4(NH_2)_2^+$
233.9013	233.8981	77	$Fe_2(NO)_3(NH_2)_2^+$
203.9032	203.9031	50	$Fe_2(NO)_2(NH_2)_2^+$
173.9062	173.9063	97	$Fe_2(NO)(NH_2)_2^+$
143.9073	143.9058	100	$Fe_2(NH_2)_2^+$
126.8812	126.8810	73	$Fe_2(NH)^+$
125.8749	125.8739	30	Fe_2N^+
112.8779	112.8778	7	Fe_2H^+
111.8698	111.8687	13	Fe_2^+
101.9516	101.9492	8	$Fe(NO)(NH_2)^+$

[a] The assignments involve the most abundant naturally occurring isotopes, i.e., ^{56}Fe, in each fragment.

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processes and that an NH_3 group is lost by the remaining $Fe_2(NH_2)_2^+$ ion (cf. Table I). The strength of the amide bridges in the complex is also indicated by the fact that $Fe_2(NO)_4(NH_2)_2$ is not cleaved by nitric oxide under ambient conditions whereas the corresponding halo dimers, $[Fe(NO)_2X]_2$, readily convert to $Fe(NO)_3X$ in the presence of NO.

It is likely that the diamido complex was first prepared in 1960 by reaction[30] 15 although at that time both the starting

$$Fe_2(CO)_6(NH_2)_2 + 4NO \xrightarrow{\text{benzene}} Fe_2(NO)_4(NH_2)_2 + 6CO \quad (15)$$

material and product were incorrectly formulated as $Fe_2(CO)_6(NH)_2$ and $Fe_2(NO)_4(NH)_2$, respectively. Subsequent X-ray and mass spectrometric studies of the carbonyl reactant established its true identity and led the investigators to suggest that the nitrosyl product of reaction 15 is also probably a diamido species.[31] Our comparison of the spectral properties displayed by an authentic sample of $Fe_2(NO)_4(NH_2)_2$ with those reported for "$Fe_2(NO)_4(NH)_2$" supports such a view.

For both the chromium amido complexes described in section d and $Fe_2(NO)_4(NH_2)_2$, we have found no evidence for the interconversion of NO and NH_2 ligands. However, unlike for $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2$, we have observed that the iron dimer does react further with I to produce as yet unidentified nitrosyl-containing products. Further studies of this and related reactions with carbanions are currently in progress.

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Registry No. I, 22722-98-1; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_3)$, 73199-26-5; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, 36607-01-9; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(NO_2)$, 68013-60-5; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2(CO)]PF_6$, 69439-82-3; $(\eta^5\text{-}C_5H_5)Cr(NO)_2(\eta^1\text{-}C_5H_5)$, 68013-59-2; $(\eta^5\text{-}C_5H_5)Cr(NO)_2I$, 53504-57-7; $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]BF_4$, 73199-25-4; $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$, 69120-55-4; $[(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]_2$, 12193-64-5; $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)(PPh_3)I$, 69120-58-7; $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)(PPh_3)H$, 73199-24-3; $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$, 66795-25-3; $[(\eta^5\text{-}C_5H_5)Co(NO)]_2$, 51862-20-5; $(\eta^5\text{-}C_5H_5)W(NO)I_2[P(OPh)_3]$, 73199-12-9; $(\eta^5\text{-}C_5H_5)Co(NO)I$, 33114-12-4; $(\eta^5\text{-}C_5H_5)W(NO)(H)(I)[P(OPh)_3]$, 73199-23-2; $[(\eta^5\text{-}C_5H_5)W(NO)I_2]_2$, 71341-43-0; $[(\eta^5\text{-}C_5H_5)W(NO)H(I)]_2$, 73199-22-1; $[(\eta^5\text{-}C_5H_5)Mo(NO)I]_2$, 37368-74-4; $[(\eta^5\text{-}C_5H_5)Mo(NO)I_2]_2$, 12203-25-7; $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)_2$, 57673-35-5; $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2)$, 39722-97-9; $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$, 12071-51-1; $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_2(NH_2)(OH)$, 73199-21-0; $[Fe(NO)_2Cl]_2$, 21576-91-0; $Fe_2(NO)_4(NH_2)_2$, 73199-20-9; $Fe(NO)_3Cl$, 14972-71-5.

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Regiospecific Substitution of Trialkylphosphines for Carbon Monoxide in Hydridoorganoruthenium Clusters

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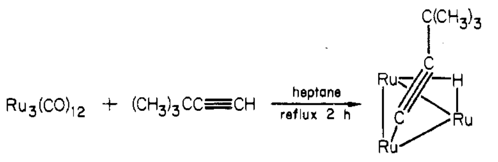
The reaction of two structural types of hydridoorganoruthenium clusters $HRu_3(CO)_9(C_6H_9)$ (I) and $HRu_3(CO)_9(C_5H_7)$ (IIa, IIb) with triphenylphosphine and trimethyl phosphite have been studied. The major product for both structural types is a monophosphine derivative (I → III; IIa → V; IIb → VI) in which a carbonyl group has been replaced only on ruthenium atoms having a σ bond with the organic ligand. Solution structures are assigned on the basis of variable-temperature ^{13}C and ^1H NMR studies. In III, only conformers with the phosphine ligand in a radial position are populated from −80 to +40 °C. However, axial–radial carbonyl exchange at the substituted ruthenium atom occurs at about the same rate as in I. A bis(phosphine) derivative of I has also been isolated and characterized (IV).

Introduction

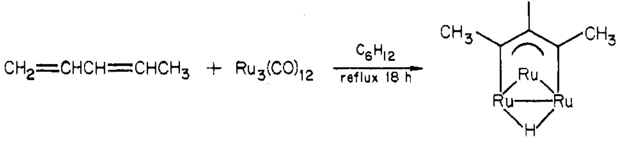
Synthetic routes to a variety of organometallic derivatives of $Ru_3(CO)_{12}$ make possible systematic investigations of the chemistry of an organic molecule bound to a trimetallic site.[1] In the case of *tert*-butylacetylene, μ_2-hydrido-$\mu_1\sigma^1,\mu_2\pi^4$-(*tert*-butylacetylido)-triruthenium nonacarbonyl (I) is isolated in 80% yield[2] (eq 1). This reaction is general for acetylenes with bulky, functionalized groups α to the triple bond where yields of 50–60% are obtained.[3]



I

(1)

A variety of dienes yield single trimetallic products when reacted with $Ru_3(CO)_{12}$, and construction of isomeric organometal derivatives with systematic structural variations is now possible. Both isoprene and 1,3-pentadiene give μ_2-hydrido-1,3-di-$\mu_1\sigma^1,\mu_2\pi^3$-allyl complexes in 35 and 50% yields, respectively[4] (eq 2a and 2b). An inspection of the solid-state



IIa

(2a)

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