Nitrosyl Transfer Reactions

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Abstract: Intermolecular transfer of the nitrosyl ligand in $CoNOD_2$ (D = monoanion of dimethylglyoxime) to $FeCl_2L_2$, $CoCl_2L_2$, $CoNOCl_2L_2$, $NiCl_2L_2$, $RuCl_2L_4$, $RuHClL_3$, $RuHNOL_3$, $RhHCOL_3$, $RuNOClL_2$, and $RhClL_3$ ($L = PPh_3$) and to $FeHCl(dpe)_2$, $FeH(THF)(dpe)_2^+$, and $FeCl_2dpe$ (dpe = 1,2-bis(diphenylphosphino)ethane) has been shown to occur. The reaction occurs more readily if the nitrosyl acceptor is coordinatively unsaturated. In some instances, chloride, hydride, or phosphine ligands migrate from the nitrosyl acceptor complex to cobalt. Halogenation of low-valent nitrosyl complexes by $CoClD_2(PPh_3)$ is also observed.

Intermolecular transfer of coordinated ligands is a reaction of some generality. Halide transfer is well known.[1] In a preliminary communication of some of the present work, we cited examples of CO transfer.[2] Alkyl transfer occurs from cobaloximes to Co(II) and Hg(II), in both instances with inversion at carbon.[3] Methyl transfer also occurs to highly nucleophilic $CpFe(CO)_2^-$.[4] Redistribution of coordinated phosphines has also been effected,[5] as has transfer of π-cyclopentadienyl,[6] π-allyl,[7] dithiolene,[8] and β-diketonate[9] ligands. Both carbene[10] and carbyne[11] ligands can migrate. We report here the results of a study of reactions involving intermolecular transfer of the nitrosyl group.

Experimental Section

All operations were carried out under N_2 using Schlenk techniques. Benzene and THF were dried with NaK alloy and ethanol with $Mg(OEt)_2$. NO was used directly from a lecture bottle. Elemental analyses were determined by Schwarzkopf Microanalytical Laboratories. Proton NMR spectra were recorded on a Varian HR-220 spectrometer and ^{31}P NMR spectra on a Varian XL-100 instrument (Fourier transform) at 40.5 MHz. Positive ^{31}P chemical shifts are downfield of the reference (85% H_3PO_4).

$CoNOD_2 \cdot MeOH$ (I). $Co(O_2CCH_3)_2 \cdot 4H_2O$ (2.5 g) and 2.3 g of dimethylglyoxime (HD)[12] were stirred under nitrogen in 50 ml of methanol, producing a red precipitate of $CoD_2 \cdot 2H_2O$.[13] Nitric oxide was bubbled through the vigorously stirred solution for 10–15 min. The red solid was replaced by a dark brown solid. After treatment with NO was terminated, the solution was cooled to −78° for 30 min. The product was rapidly filtered cold: yield, 2.88 g (82%); ν(NO) 1645 and, sometimes, 1705 cm^{-1} (Nujol) with varying relative intensities. Anal. Calcd for $C_9H_{18}N_5CoO_6$: C, 30.80; H, 5.13; N, 19.94. Found: C, 30.58; H, 5.13; N, 20.59. The sample analyzed showed only the 1645 cm^{-1} frequency: proton NMR (in $CDCl_3$) δ 2.45 (CH_3 of dimethylglyoximate), 3.35 (CH_3 of methanol), 11.7 (OH of dimethylglyoximate). The product should not be washed with water (compare ref 14) since it is appreciably soluble in that solvent.

$FeCl_2(PPh_3)_2$. Following the reported method,[15] 2.81 g (22 mmol) of $FeCl_2$ and 17.25 g (66 mmol) of PPh_3 were refluxed in 60 ml of benzene for 17 h. The solution was filtered hot. Upon cooling, the colorless product precipitated. The product did not melt under vacuum below 300°.

$FeCl_2dpe$. According to the method reported[16] for "$FeCl_2(dpe)_2$", anhydrous $FeCl_2$ (0.19 g, 1.54 mmol) and dpe[12] (1.10 g, 2.76 mmol) were refluxed in 25 ml of benzene for 26 h. The solution was filtered hot to remove 0.05 g of $FeCl_2$. The solution was concentrated to 10 ml, 10 ml of pentane was added slowly, and the solution was stirred for 3 h. The colorless solid which formed was filtered, washed with 5 ml of pentane, and dried, mp (under vacuum) 236–242°. Anal. Calcd for $C_{26}H_{24}FeCl_2P_2$: C, 59.45; H, 4.57; Cl, 13.5; P, 11.81. Found: C, 59.65; H, 4.64; Cl, 12.43; P, 11.54.

$NiCl_2(PPh_3)_2$ + I. $NiCl_2(PPh_3)_2$ (0.654 g, 1.0 mmol) and I (0.351 g, 1.0 mmol) were stirred at 25° in 20 ml of THF. No PPh_3 was added. After 2 h a new nitrosyl stretching frequency was present at 1722 cm^{-1} ($Ni_2(NO)_2Cl_2(PPh_3)_2$).[17] Eighteen hours later, the band due to I was very weak, but bands were present at 1722 and 1744 cm^{-1}, the latter due to $Ni(NO)Cl(PPh_3)_2$.[17] The volume was reduced to 5 ml, and filtration separated 0.44 g (75% yield) of $CoClD_2(PPh_3)$ (II), identified by proton NMR and ir. Addition of benzene to the green THF filtrate produced dark crystals which were shown by ir and elemental analysis to be a 2:1 mixture of $NiNOCl(PPh_3)_2$ and $[NiNOCl(PPh_3)]_2$. This mixture was refluxed in benzene with 0.1 g of PPh_3, to produce needle crystals of $NiNOCl(PPh_3)_2$ (ν(NO) = 1726 cm^{-1} in KBr, mp 205–210°); no trace of the halide bridged dimer remains.

$CoCl_2(PPh_3)_2$ + I. $CoCl_2(PPh_3)_2$ (1.5 g, 2.29 mmol), I (0.80 g, 2.28 mmol), and PPh_3 (0.60 g, 2.29 mmol) were slurried together in 55 ml of ethanol at 25°. After 2 h, the solution was green-black and showed absorptions at 1834, 1785, and 1743 cm^{-1} characteristic[18] of a mixture of $Co(NO)_2L_2^+$ and $Co(NO)_2ClL$. The solution was filtered and the separated solid washed with 4 ml of EtOH. The combined filtrate was evaporated to dryness for later workup (below). The solid separated in this initial filtration was washed repeatedly (15 × 4 ml) with benzene to remove red $CoD_2(PPh_3)$. The last few washings came off pale yellow, and left behind a gold solid. This solid was recrystallized from $CHCl_3$/benzene and characterized by ir, ^1H NMR, and elemental analysis as $CoClD_2(PPh_3) \cdot C_6H_6$.

The green solid, produced upon vacuum drying the initial ethanol filtrate, showed only two nitrosyl stretches (1851 and 1790 cm^{-1} in KBr) as a result of phosphine substitution on $Co(NO)_2Cl(PPh_3)$ as the solution was concentrated. The dinitrosyl cation was therefore precipitated by adding 0.41 g of $NaBPh_4$ in 6 ml of EtOH to a homogeneous solution of the green solid in 5 ml of EtOH. $[Co(NO)_2(PPh_3)_2]BPh_4$ was identified by its ir and ^{31}P NMR spectra.

$CoNOCl_2(PPh_3)_2$ + I. $CoNOCl_2(PPh_3)_2$[19] (0.624 g, 0.913 mmol), I (0.32 g, 0.91 mmol), and PPh_3 (0.24 g, 0.91 mmol) were stirred at 25° in 20 ml of ethanol. After 14.5 h, the ir spectrum showed bands due to $Co(NO)_2L_2^+$ and $Co(NO)_2ClL$. The solution was concentrated to 10 ml and filtered, and the separated solid was washed with 3 × 2 ml of ethanol to leave a pale yellow solid (0.51 g, 95% yield). This solid was recrystallized from $CHCl_3$/benzene to yield $CoClD_2PPh_3 \cdot C_6H_6$. Anal. Calcd for $C_{32}H_{35}ClCoN_4O_4P$: C, 57.74; H, 5.26; Cl, 5.34. Found: C, 57.03; H, 4.99; Cl, 5.26. To the green filtrate from the initial filtration of the reaction solution was added 0.35 g of $NaBPh_4$ in 5 ml of ethanol. The resulting brown solid (0.75 g, 86%) was filtered, washed with 3 × 3 ml of ethanol, and vacuum dried. Recrystallization of this solid from $CHCl_3$/MeOH/Et_2O produced 0.67 g of dark crystals of $[Co(NO)_2(PPh_3)_2]BPh_4$: ν(NO) 1861 and 1796 cm^{-1}. Anal. Calcd for $C_{60}H_{50}BCoN_2O_2P_2$: C, 74.84; H, 5.24; N, 2.91. Found: C, 74.63; H, 5.43; N, 3.33.

$RuCl_2(PPh_3)_4$ + I. $RuCl_2(PPh_3)_4$[20] (0.043 g, 0.035 mmol) and I (0.025 g, 0.07 mmol) were degassed and stirred in 3 ml of EtOH for 3.5 h at 25°. The solution was filtered and the resultant solid was washed with three 1-ml portions of Et_2O. The ir spectrum showed this to be approximately equimolar $RuNOCl_3(PPh_3)_2$[21] and $RuNOCl(O_2)(PPh_3)_2$.[22] The latter could be extracted from the former with benzene and crystallized with methanol. Anal. Calcd for $C_{36}H_{30}NClNO_3Ru$: C, 59.75; H, 4.15; N, 1.94. Found: C, 59.75; H, 4.40; N, 2.10.

$RhCl(PPh_3)_3$ + I. $RhCl(PPh_3)_3$[23] (0.1 g, 0.108 mmol) and I (0.038 g, 0.108 mmol) were stirred in 2.5 ml of benzene at 25°. The solution color changes from an initial red-brown to deep red and after 1.5 h, a new nitrosyl stretch due to $RhNO(PPh_3)_3$ is evident at 1625 cm^{-1}. Simultaneously, pale yellow solid forms. After a total reaction time of 5 h, the solution was filtered. The solid separated here was washed with two 2-ml portions of $CHCl_3$ and shown to be $RhNOCl_2(PPh_3)_2$ by comparison to an authentic sample,[21] yield (based on Cl) 0.035 g (90%). The initial benzene filtrate was concentrated to ~1 ml and methanol was slowly added. Careful recrystallization from benzene/methanol produced 0.045 g of $RhNO(PPh_3)_3$ as dark red prisms, yield (based on residual NO) 92%.

$RhNO(PPh_3)_3$ + II. $RhNO(PPh_3)_3$[21] (0.05 g, 0.054 mmol) and II (0.063 g, 0.108 mmol) were stirred in 4 ml of benzene at 25°. After 3 h, the solution was filtered. The separated solid was washed with 3 ml of benzene, then three 1-ml portions of $CHCl_3$, and vacuum dried. It was identified by ir as $RhNOCl_2(PPh_3)_2$, yield 0.04 g (100%).

$HRhCO(PPh_3)_2$ + I. (a). An exploratory reaction was run in a sealed evacuated NMR tube and monitored by ^{31}P NMR. Products were identified by comparison with authentic samples. $HRhCO(PPh_3)_3$[21] (0.05 g, 0.054 mmole) and I (0.02 g, 0.054 mmol) were allowed to react at 25° in 0.5 ml of THF. After 14 h, the solution contained 26% unreacted $HRhCO(PPh_3)_3$ (39.9 ppm, J_{Rh-P} = 155 Hz), 62% $RhNOCO(PPh_3)_2$[24] (46.8 ppm, J_{Rh-P} = 164 Hz), and 12% $RhNO(PPh_3)_3$ (51.8 ppm, J_{Rh-P} = 172 Hz). After 84 h, the phosphorus NMR spectrum showed 96% $RhNOCO(PPh_3)_2$ and 4% $RhNO(PPh_3)_3$. A very broad resonance at 55.2 ppm is attributed to phosphorus bound to cobalt.

(b). $HRhCO(PPh_3)_3$ (1.02 g, 1.11 mmol) and 0.39 g of I (1.11 mmol) were stirred at 25° for 14 h in 25 ml of THF. The solvent was removed under vacuum and the dry solid was extracted with 10 ml of THF. Addition of 20 ml of hexanes followed by filtration yielded a brown solid composed mainly of $RhNOCO(PPh_3)_2$ (ν(NO) 1655 cm^{-1}; ν(CO) 1960, 1935 cm^{-1}, Nujol) along with a trace of I. The THF/hexane filtrate contains unreacted $HRhCO(PPh_3)_3$, $RhNOCO(PPh_3)_2$, and $RhNO(PPh_3)_3$.

$HRhCO(PPh_3)_3$ + *N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide. $HRhCO(PPh_3)_3$ (0.02 g) and the sulfonamide (0.005 g) were dissolved in 0.5 ml of THF in an NMR tube and allowed to react for 15 min. The solution was then held at −196° until it was assayed by ^{31}P NMR.

$RuHCl(PPh_3)_3$ + I. $RuHCl(PPh_3)_3$[25] (0.16 g, 0.17 mmol), I (0.06 g, 0.17 mmol), and PPh_3 (0.05 g, 0.17 mmol) were stirred at 25° in 15 ml of THF for 14 h. After filtering, addition of methanol to the concentrated filtrate precipitated $Ru(NO)_2(PPh_3)_2$, yield 70% based on NO. A trace of $Co(NO)_2Cl(PPh_3)$ is also produced.

$RuHNO(PPh_3)_3$ and I. $RuHNO(PPh_3)_3$[26] (0.6 g, 0.65 mmol), I (0.23 g, 0.65 mmol), and 0.17 g (0.65 mmol) of PPh_3 were stirred at 25° for 13 h in 20 ml of THF (the reaction was not yet complete after 4 h). Solid was filtered off and methanol added to the concentrated filtrate to precipitate $Ru(NO)_2(PPh_3)_2$, identified by its ir spectrum, yield 88%. A small amount of $Co(NO)_2Cl(PPh_3)$ was present in the filtrate.

$RuNOCl(PPh_3)_2$ + I. To 0.65 g (0.94 mmol) of $RuNOCl(PPh_3)_2$[27] and 1 equiv of PPh_3 in 20 ml of benzene was added 0.33 g (0.94 mmol) of I in 20 ml of benzene. Reaction was complete in 1.5 h at 25°. After a total of 6 h, the reaction was filtered. The solid so obtained was shown by ir spectroscopy to consist of II and $RuNOCl_3(PPh_3)_2$ (ν(NO) 1875 cm^{-1}). Solvent was stripped from the filtrate, and the residual solid was extracted with 5 ml of THF. $Ru(NO)_2(PPh_3)_2$ was precipitated from the THF extracts by addition of methanol (25 ml). The dark red dinitrosyl was recrystallized from THF/methanol, yield 70%. Anal. Calcd for $C_{36}H_{30}N_2O_2P_2Ru$: C, 63.01; H, 4.37; P, 9.03; N, 4.08. Found: C, 62.53; H, 4.57; P, 8.90; N, 4.69. ν(NO) 1660, 1615 cm^{-1} (CH_2Cl_2). Only trace amounts of $Co(NO)_2Cl(PPh_3)$ are produced.

$Ru(NO)_2(PPh_3)_2$ + II. $Ru(NO)_2(PPh_3)_2$ (0.05 g, 0.07 mmol) and II (0.13 g, 0.21 mmol) were stirred in 5 ml of THF at 25° for 8 h. Filtration yielded a brown solid composed of $RuNOCl_3(PPh_3)_2$ (ν(NO) 1875 cm^{-1}, Nujol) and a dmg complex. The filtrate was taken to dryness; $CoNOD_2$ was extracted away from 0.02 g of unreacted $Ru(NO)_2(PPh_3)_2$ with methanol, and was identified by ir and proton NMR spectra. Even after reaction times of 15–18 h, approximately the same amount of unreacted $Ru(NO)_2(PPh_3)_2$ remains.

Reaction of $FeCl_2(PPh_3)_2$ with I. (1). $CoNOD_2{\cdot}CH_3OH$ (0.70 g, 1.98 mmol), $FeCl_2(PPh_3)_2$ (0.644 g, 0.99 mmol), and PPh_3 (0.519 g, 1.98 mmol) were stirred at 25° in 15 ml of THF for 7 h. $CoClD_2(PPh_3)$ (II) was removed by filtration and identified by its infrared spectrum. The filtrate was concentrated to a volume of several milliliters. Addition of methanol produced brown-black crystals of $Fe(NO)_2(PPh_3)_2$ (0.36 g, 58% yield). Anal. Calcd for $C_{36}H_{30}N_2FeO_2P_2$: C, 67.51; H, 4.68; P, 9.70; N, 4.37. Found: C, 65.39; H, 5.23; P, 9.81; N, 4.66. ν(NO) 1720, 1675 cm^{-1} (THF). The filtrate from this second filtration exhibited an ir spectrum characteristic of a 2:1 mixture of $Co(NO)_2Cl(PPh_3)$ (ν(NO) 1810, 1760, 1730 cm^{-1}, Nujol) and $Fe(NO)_2(PPh_3)_2$, along with a trace of I. Attempts to isolate the cobalt dinitrosyl produced an oil. It was therefore derivatized to $[Co(NO)_2(PPh_3)_2]BPh_4$ by refluxing with 0.19 g of PPh_3 in ethanol in the presence of $NaBPh_4$. Anal. Calcd for $C_{60}H_{50}N_2BCoO_2P_2$: P, 6.45. Found: P, 6.12. ν(NO) 1855, 1795 cm^{-1} (Nujol). After removal of the cobalt dinitrosyl, the filtrate gave a positive test for free dimethylglyoximate. Combining the results from the various fractions, the basic reaction produces $Fe(NO)_2(PPh_3)_2$ and $Co(NO)_2Cl(PPh_3)$ in approximately a 3:1 mole ratio.

(2). $FeCl_2(PPh_3)_2$ (0.022 g), I (0.024 g), and PPh_3 (0.018 g) were sealed in an NMR tube with 0.5 ml of THF. After 17 h at 25°, the ^{31}P NMR spectrum (−64°) exhibited (among others) a resonance at 47.6 ppm, which duplicates the chemical shift of an authentic sample of $Co(NO)_2Cl(PPh_3)$ at this same temperature.

Fifteen minutes after initiating the above reactions, an ir absorption was evident at 1775 cm^{-1} in THF. By the end of 75 min, absorptions due to the iron and cobalt dinitrosyls were evident. Reactions 3–6 were run to identify the source of the 1775-cm^{-1} band.

(3). To 1.24 g (1.9 mmol) of $FeCl_2(PPh_3)_2$ and 0.50 g (1.9 mmol) of PPh_3 in 5 ml of THF was added, within 7 min, 0.70 g (2.0 mmol) of I in 7 ml of THF. The ir spectrum at this point showed the 1775-cm^{-1} band along with those of I, $Fe(NO)_2(PPh_3)_2$, and $Co(NO)_2Cl(PPh_3)$. The ratio of the intensity of the 1775-cm^{-1} band to one of those of $Fe(NO)_2(PPh_3)_2$ was 1:4. After 10 min of additional stirring, a solid was filtered and washed with THF; this solid contained only the unknown nitrosyl and II. No successful separation of the two components of this solid was achieved.

(4). $FeCl_2(PPh_3)_2$ (0.60 g, 0.91 mmol), I (0.32 g, 0.91 mmol), and PPh_3 (0.24 g, 0.91 mmol) were stirred for 4 min in 4 ml of THF. The solution was then filtered and the filtrate rapidly taken to dryness. The solid on the filter disk was washed with 10 ml of methanol and dried. An ir spectrum (Nujol) of this filtered solid showed it to consist of the unknown complex, $Fe(NO)_2(PPh_3)_2$, and a small amount of $CoNOD_2$. $Co(NO)_2Cl(PPh_3)$ is absent but insoluble II is presumably present. The ir spectrum of this solid, redissolved in THF, was monitored for 55 min. Immediately after preparing this solution, $Co(NO)_2Cl(PPh_3)$ was evident, and continues to grow during the duration of the experiment. In this same time period, $CoNOD_2$ and the unknown mononitrosyl disappear. The growth of $Co(NO)_2Cl(PPh_3)$ and the decay of $CoNOD_2$ appear to be simultaneous independent occurrences, however. In contrast, the initial filtrate, which contained $Co(NO)_2Cl(PPh_3)$, $Fe(NO)_2(PPh_3)_2$, and the unknown mononitrosyl showed no spectral changes over 40 min after redissolution in THF.

(5). $FeCl_2(PPh_3)_2$ (1.30 g, 1.97 mmol), I (0.17 g, 0.49 mmol), and PPh_3 (0.13 g, 0.49 mmol) were intimately mixed as solids. THF (7 ml) was added and the solution stirred for 25 min. At this point, $Fe(NO)_2(PPh_3)_2$ was the only nitrosyl evident (ir evidence).

(6). $FeCl_2(PPh_3)_2$ (1.35 g, 2.1 mmol) and $Fe(NO)_2(PPh_3)_2$ (1.32 g, 2.1 mmol) were refluxed in THF for 17 h. Infrared spectroscopy showed that no reaction occurred.

In order to ascertain the origin of the $Co(NO)_2Cl(PPh_3)$ produced in the above reactions, the following two reactions were carried out.

$Fe(NO)_2(PPh_3)_2$ + II. $Fe(NO)_2(PPh_3)_2$ (0.50 g, 0.77 mmol) and II (0.46 g, 0.78 mmol) were stirred for 20 h in 25 ml of THF at 25°. The ir spectrum of the solution at this time showed evidence for $Co(NO)_2Cl(PPh_3)_2$ and $Co(NO)_2(PPh_3)_2{}^+$ (combined yield 40%) as well as $CoNOD_2$ and unreacted $Fe(NO)_2(PPh_3)_2$ (combined yield 60%). $Fe(NO)_2(PPh_3)_2$ (0.22 g, 44%) and II (0.19 g, 41%) were recovered. The $Co(NO)_2Cl(PPh_3)$ was derivatized to $[Co(NO)_2(PPh_3)_2]BPh_4$ and identified by its infrared spectrum.

I and II. Compound I (0.048 g) and compound II (0.04 g) were stirred in 2 ml of THF for 4 h. An infrared spectrum of the reaction solution shows a nitrosyl absorption due solely to I, indicating no net reaction.

FeHCl(dpe)$_2$ + I. (1). FeHCl(dpe)$_2$[16] (0.90 g, 1.0 mmol) and I (0.356 g, 1.0 mmol) react (ir evidence) to only a small extent after 96 h of stirring in 15 ml of THF at 25°. The reaction was therefore refluxed for 14 h. After cooling to 25°, the THF was removed under vacuum and the residual solid extracted with hot ethanol. After filtering, $Fe(NO)_2$dpe crystallized on standing from the ethanol solution. The dinitrosyl was recrystallized from acetone/ethanol, yield 40% based on NO. Anal. Calcd for $C_{26}H_{24}N_2FeO_2P_2$: C, 60.72; H, 4.67; P, 11.85;

N, 5.45. Found: C, 60.82; H, 4.72; P, 11.75; N, 5.70. ν(NO) 1675, 1725 (THF). A separate experiment proved that the rate and yield of this reaction were unaffected by addition of 10 mol % of $CoD_2 \cdot 2H_2O$.

(2). $FeHCl(dpe)_2$ (0.20 g, 0.23 mmol) and **I** (0.08 g, 0.23 mmol) were stirred at room temperature in 7 ml of benzene for 72 h. Infrared evidence showed that $Fe(NO)_2dpe$ formation was approximately 33% complete at this point. The reaction was then refluxed for 14 h, cooled to 25°, and filtered. This filtered solid showed vibrations characteristic of DMG, and was insoluble in all common organic solvents. The filtrate above was pumped to dryness and extracted with acetone to separate $Fe(NO)_2dpe$ (soluble) from $FeHCl(dpe)_2$ (insoluble). Addition of ethanol to the concentrated acetone solution precipitated brown $Fe(NO)_2dpe$.

(3). $FeHCl(dpe)_2$ (0.31 g, 0.34 mmol), I (0.12 g, 0.34 mmol), and NH_4PF_6 (0.05 g, 0.34 mmol) were unreactive at 25° in 20 ml of ethanol over a period of 12 h. The mixture was then refluxed for 4 h, cooled, and filtered. Upon standing, a small amount of green solid formed; this was identified as $[FeNO(dpe)_2]PF_6$[28] by ir (ν(NO) 1680 cm^{-1}, Nujol) and ^{31}P NMR (81.5 ppm), yield 11%. The filtrate contained $Fe(NO)_2dpe$.

(4). $FeHCl(dpe)_2$ (0.4 g, 0.45 mmol) and I (0.16 g, 0.45 mmol) were stirred at 25° in 12 ml of CH_3CN for 16 h. The solvent was removed under vacuum. An ir spectrum of a THF extract of the residue showed only a single nitrosyl band at 1607 cm^{-1}, due to $CoNOD_2Cl^{-1}$. Metal hydride (1860 cm^{-1}) and coordinated acetonitrile (2235 cm^{-1}) bands due to $FeHdpe_2(CH_3CN)^+$ are also evident.[29] No product due to nitrosyl transfer was present.

$[FeH(dpe)_2(THF)]BPh_4$ + I. $FeHCl(dpe)_2$ (0.70 g, 0.79 mmol) and $NaBPh_4$ (0.27 g, 0.79 mmol) were stirred in 13 ml of THF under argon for 8 h. This produces a precipitate of $[FeH(dpe)_2(THF)]BPh_4$.[29] To this slurry was added 0.28 g (0.79 mmol) of I in 9 ml of THF. Stirring at 25° was continued for 13 h. The THF was then removed under vacuum and the dry solid residue extracted with 15 ml of acetone. In the course of concentrating the filtered extracts, a trace (0.03 g) of red $FeHCl(dpe)_2$ precipitated and was filtered off. The infrared spectrum of this filtrate showed $Fe(NO)_2dpe$ to be the only nitrosyl species formed in the reaction. Bubbling nitrogen gas through this solution generated a new stretching frequency at 2130 cm^{-1} characteristic[29] of $FeH(N_2)(dpe)_2{}^+$; this confirms the successful formation of $FeH(dpe)_2THF^+$ in the first phase of this reaction.

$[FeNO(dpe)_2]Cl$ + I. $[FeNO(dpe)_2]Cl$[30] (0.14 g, 0.15 mmol) and I (0.05 g, 0.15 mmol) were unreactive in 6 ml of THF at 25° in a 3-h period. Refluxing for 11 h produced only $Fe(NO)_2dpe$, identified by its infrared spectrum.

$[FeNO(dpe)_2]PF_6$ + I. $[FeNO(dpe)_2]PF_6$[28] (0.11 g, 0.11 mmol) and I (0.04 g, 0.11 mmol) in 7 ml of THF did not react at 25° in 12 h. The solution was refluxed for 11 h, cooled, and filtered. The solid filtered off here shows infrared evidence for $PF_6{}^-$, phenyl groups, and DMG. It was insoluble in all common organic solvents. Although no completely acceptable analysis was obtained, the atom ratios from the observed analysis (C:H:N:P = 34.2:41.2:4.22:3.0) are consistent with $[CoD_2dpe]PF_6$. Anal. Calcd for $C_{34}H_{38}N_4CoF_6O_4P_3$: C, 49.09; H, 4.57; N, 6.73; P, 11.18. Found: C, 44.01; H, 4.42; N, 6.35; P, 9.99. The only nitrosyl in the THF filtrate from above was $Fe(NO)_2dpe$, identified by ir and ^{31}P NMR spectroscopy (79.2 ppm).

$FeCl_2dpe$ + I. To 0.11 g (0.21 mmol) of $FeCl_2dpe$ in 5 ml of THF was added 0.04 g (0.12 mmol) of I and 0.02 g (0.12 mmol) of NH_4PF_6 in 5 ml of THF. A brown solid formed immediately. After 2 h stirring, the solution was filtered. The filtrate was concentrated to 1–2 ml and methanol added to precipitate the nitrosyl products, shown by ir and ^{31}P NMR to be $[FeNO(dpe)_2]PF_6$ (81.7 ppm) and $Fe(NO)_2dpe$ (79.1 ppm). By phosphorus NMR, these two nitrosyl complexes are produced in a mole ratio of 1:2.

Results

The Transfer Reagent, $Co(NO)D_2 \cdot MeOH$. A methanolic solution of CoD_2PPh_3[13] rapidly reacts with NO to produce a mononitrosyl species exhibiting an NO stretching vibration at 1640 cm^{-1}. The isolated product analyzes as the 1:1 solvate $CoNOD_2 \cdot MeOH$, and the proton NMR in $CDCl_3$ exhibits a methoxy methyl resonance with one-quarter of the intensity of the dimethylglyoximate methyl groups. If the reaction is run by passing NO through a 1:2 mixture of cobalt(II) acetate and dimethylglyoxime, the reaction time must be carefully controlled to prevent oxidation, by NO, to $Co(NO_2)D_2 \cdot$solvent. We find the 2-h reaction time quoted in ref 14 to produce large amounts of nitro complex. Oxidation of $CoNOD_2 \cdot MeOH$ (I) by free NO is known,[31] but requires basic conditions. Apparently the acetate ion functions as the base in this complicating side-reaction. The solid-state infrared spectrum of I shows ν(NO) at 1639 cm^{-1}. Also present is a broad absorption at 2325 cm^{-1}. The nitrosyl stretching frequency undergoes a remarkably large shift to higher energy in noncoordinating solvents; in $CHCl_3$ ν(NO) is 1717 cm^{-1}. Moreover, the proton NMR shows a resonance for methanol C–H protons which superimposes on added methanol. This is consistent with complete dissociation of methanol to produce five-coordinate $CoNOD_2$ in $CHCl_3$. Two further observations support this contention. Periodically, we have synthesized samples of I which show two nitrosyl frequencies in the solid state. Proton NMR shows such samples to be deficient in methanol, the degree of deficiency correlating with the intensity of the higher energy ir band (1704 cm^{-1}, in Nujol). Finally, heating stoichiometric $CoNOD_2 \cdot MeOH$ under vacuum for 20 h yields a solid exhibiting two equally intense nitrosyl bands. Azeotropic distillation of methanol/benzene from $CoNOD_2 \cdot MeOH$ in benzene produces the same result. In $CHCl_3$, the methanol-deficient material shows only the 1717-cm^{-1} nitrosyl band. As methanol is removed from the solid, the 2325-cm^{-1} band declines in intensity. We feel this is the O–H stretching vibration of coordinated methanol which also participates in hydrogen bonding either to (a) the nitrosyl group of a neighboring molecule or (b) a dimethylglyoximate oxygen. Examples of hydrogen bonding of lattice-trapped solvent to both functionalities are known.[32,33] The compound $CoD_2(CH_3)H_2O$ also exhibits such an infrared absorption, and it too disappears in anhydrous analogues.[34]

$CoNOD_2 \cdot MeOH$ is soluble in a wide variety of solvents, ranging from water to benzene. When pure, it is oxidized by O_2 to a nitro (and possible nitrate[35]) complex within 1 day in $CHCl_3$ solution, but is air stable as a solid. It may be recovered unchanged after 10 h at reflux in THF, indicating that there is no tendency to dissociate NO. In view of the similarity of the nitrosyl stretching frequency of I to that in a number of authentic bent nitrosyl complexes,[2] the CoNO moiety is presumably bent in I.

Among bent nitrosyl complexes of Co, Rh, and Ir, only cobalt shows evidence for coordination of groups trans to the nitrosyl. In every instance, the bonds so formed are very long, due presumably to the trans effect of "bent NO". The ready loss of coordinated methanol by I is therefore understandable. Proton NMR spectra of I in CH_2Cl_2 as low as −90° show no evidence for dimerization via the oxime oxygens. $CoCH_3D_2$ is wholly dimeric under these conditions,[36] indicating that the nitrosyl group has a very high trans effect.

Infrared spectroscopy provides clear evidence for adduct formation by five-coordinate $CoNOD_2$ with certain bases (Table I). The methanol adduct apparently persists intact in methanol solution. Pyridine, THF, PPh_3, and acetonitrile also coordinate. Chloride and iodide also bind, producing in some solvents an equilibrium mixture of $CoNOD_2$ and $CoNOD_2X^-$. Removal of solvent from an acetonitrile solution of $[Ph_4As]Cl$ and I yields a solid, presumably a $Co(NO)D_2Cl^{-1}$ salt, with a nitrosyl frequency of 1588 cm^{-1} (Nujol).

Clarkson and Basolo have analyzed kinetic data on the oxidation of CoNO(L) complexes in terms of the formation of base adducts.[37] L included Schiff bases and dithiocarbamates, but not dimethylglyoximate. They were unable to directly detect such adducts, however. More recently, an adduct of I with a substituted pyridine was detected in solution by ir and NMR methods.[35] It was noted that dimethylglyoximate complexes generally have higher base adduct formation constants than their Schiff base analogues. The base adducts observed here are quite different from the adduct of $CoNO(das)_2^{2+}$ with SCN^-; the latter[38] involves a linear-to-bent conversion, while we consider adducts of I to involve only minor alterations of structure and electron density.

Reactions of I. (a) $NiCl_2(PPh_3)_2$. Interaction of $CoNOD_2 \cdot MeOH$ with $NiCl_2L_2$ in the absence of added phosphine produces the dimeric complex $L(ON)Ni(\mu\text{-}Cl)_2NiNOL$. The nickel has lost phosphine during the reaction, and it was found associated with cobalt. The second reaction product is $CoClD_2(PPh_3)$. The tendency for Co(III) to be six-coordinate necessitates binding of an additional ligand after chloride transfer. This can be PPh_3, but it need not be so. Thus, if the reaction of I with $NiCl_2L_2$ is left for 18 h, an equilibrium mixture of $NiNOClL_2$ and the halide-bridged dimer is produced. In this case $CoClD_2(THF)$ must form. In order to avoid the complications of phosphine scavenging by the Co(III) halide complex, equimolar PPh_3 was normally added to most nitrosyl transfers. This has the added feature of forming a poorly soluble and thus easily separated product, $CoClD_2(PPh_3)$.

(b) $CoCl_2(PPh_3)_2$. This acceptor was selected for investigation because it is a 15-electron complex. Simple transfer of neutral NO from I is thus anticipated. The expected product, $CoNOCl_2L_2$, is known. However, nitrosyl transfer to $CoCl_2L_2$, even with equimolar I, produces only $Co(NO)_2ClL$ in equilibrium with $Co(NO)_2L_2^+$. Both cobalt dinitrosyls are produced even in the absence of added phosphine, and separation of these two is difficult. Even when phosphine is added ($2PPh_3/Co(NO)_2^+$ unit), conversion to the cation is not complete since eq 1 is an equilibrium.

$$Co(NO)_2Cl(PPh_3) + PPh_3 \rightleftharpoons Co(NO)_2(PPh_3)_2^+ + Cl^- \quad (1)$$

Equation 1 can be shifted completely to the right by precipitating the salt $[Co(NO)_2(PPh_3)_2]BPh_4$.

The observed transfer of two nitrosyl groups and one chlorine atom could proceed in two ways. If simple NO transfer precedes NO/Cl redistribution, $CoNOCl_2L_2$ is an intermediate. If the reverse is true, $CoNOClL_2$ is the intermediate. The following transfer was therefore attempted.

(c) $CoNOCl_2(PPh_3)_2$. This complex reacts with equimolar I rapidly at 25° to produce the same mixture of cobalt dinitrosyls as observed above. This result is consistent with the double nitrosyl transfer to $CoCl_2L_2$ proceeding by initial simple NO transfer.

(d) $RuCl_2(PPh_3)_4$. This complex dissociates completely to produce unsaturated $RuCl_2L_3$.[39] Reaction with I produces mononitrosyl species. The expected $RuNOClL_2$ is isolated as its O_2 adduct as a result of adventitious oxygen. One-half of the nitrosyl-containing product is the trihalide $RuNOCl_3L_2$. The two ruthenium complexes account for all of the halogen, and the cobalt-containing product remains soluble as CoD_2. This stoichiometry differs from the reaction of $RuCl_2L_3$ with NO itself (eq 2).[40]

$$3RuCl_2L_3 + 4NO \rightarrow 2RuNOCl_3L_2 + Ru(NO)_2L_2 + 3L \quad (2)$$

(e) $RhCl(PPh_3)_3$. Reaction of this square planar complex with I yields two products. One is the expected $RhNOL_3$. The second is the very insoluble $RhNOCl_2L_2$. The latter is a halogen-rich product. It was shown in an independent reaction that $CoClD_2(PPh_3)$ reacts with $RhNOL_3$ to produce the rhodium dichloronitrosyl (eq 3).

$$2CoClD_2(PPh_3) + RhNO(PPh_3)_3 \rightarrow RhNOCl_2(PPh_3)_2 + 2CoD_2(PPh_3) + PPh_3 \quad (3)$$

(f) $HRhCO(PPh_3)_3$. $HRhCOL_3$, which dissociates L in solution,[41] reacts with I to produce $RhNOCOL_2$ and traces of $RhNOL_3$. Initially, we thought the production of $RhNOL_3$ was mechanistically significant in suggesting that expulsion of CO was competitive with loss of PPh_3. A separate experiment, monitored by ^{31}P NMR, showed that PPh_3 replaces CO in $RhNOCOL_2$, however. This demonstrates the existence of the following equilibrium (eq 4).

$$RhNOL_3 + CO \rightleftharpoons RhNOCOL_2 + L \quad (4)$$

The appearance of $RhNOL_3$ in the nitrosyl transfer is then attributable to PPh_3 substitution on $RhNOCOL_2$, the primary product. The observation that the $RhNOL_3/RhNOCOL_2$ ratio *falls* during the course of the reaction is presumably due to the fact that $HRhCOL_3$ dissociation causes [L] to be highest early in the reaction. As nitrosyl transfer proceeds, the $HCoD_2$ produced (see Discussion) functions as a phosphine scavenger, thereby preventing the secondary substitution reaction on $RhNOCOL_2$.

Table I. Stretching Frequencies of $Co(NO)D_2MeOH$ in Various Solvents

Solvent	ν(NO), cm^{-1}
CH_3CN, $[Ph_4As]Cl$ added[a]	1608
THF, $[N(n\text{-}Bu)_4]Cl$ added[b]	1607, 1655
$CHCl_3$, pyridine added[a]	1639
CH_2Cl_2, $[N(n\text{-}Bu)_4]I$ added[a]	1629, 1710
MeOH	1640
CH_3CN	1647
THF	1655
CH_2Cl_2, PPh_3 added	1661
C_6H_6	1686
CH_2Cl_2	1710
$CHCl_3$	1717

[a] Mole ratio added base:Co = 5:1. [b] Mole ratio added base:Co = 10:1.

By analogy to the above reaction, we find $HRhCOL_3$ to react within 15 min at 25° with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in THF to produce $RhNOCOL_2$, along with 4% $RhNOL_3$.

(g) $RuHCl(PPh_3)_3$, $RuHNO(PPh_3)_3$, and $RuNOCl(PPh_3)_2$. The compound $RuHClL_3$ provides an opportunity to compare the propensity of hydride and chloride ligands to undergo nitrosyl transfer. Reaction of $RuHClL_3$ and I in a 1:1 mole ratio produces $Ru(NO)_2L_2$ as the only ruthenium-containing nitrosyl product. This indicates that the actual mononitrosyl intermediate, either $RuHNOL_3$ or $RuClNOL_2$, reacts faster with I than does $RuHClL_3$. It was shown directly that both of these mononitrosyls do indeed undergo facile nitrosyl transfer (see Scheme I) and thus it is impossible to determine if one of the two possible nitrosyl transfer sequences (H before Cl, etc.) occurs exclusively.

Scheme I

$$RuHClL_3 + CoNOD_2 \longrightarrow \left\{\begin{array}{l} RuClNOL_2 + L \xrightarrow{CoNOD_2} Ru(NO)_2L_2 \\ \text{or} \\ RuHNOL_3 \xrightarrow{CoNOD_2} Ru(NO)_2L_2 + L \end{array}\right.$$

In a complicating side reaction, a small amount of $RuNOCl_3L_2$ is produced in the reaction of $RuNOClL_2$ with I. It was demonstrated directly that $CoClD_2L$ halogenates $Ru(NO)_2L_2$ (eq 5).[42]

$$Ru(NO)_2L_2 + 3CoClD_2L \rightarrow RuNOCl_3L_2 + CoNOD_2 + 2CoD_2 \quad (5)$$

We feel eq 5 is not actually the major source of the $RuNOCl_3L_2$ in the reaction of $RuNOClL_2$ with I, however. Instead, we prefer to base the appearance of the trichloride on direct reaction of the very sensitive $RuNOClL_2$ with $CoClD_2L$ as it is produced. Such a reaction is implicated by the products from nitrosyl transfer to $RuCl_2L_4$ (d above). We have independent evidence that $RuNOClL_2$ is halogenated by chlorocarbon solvents, and the complex is infamous for its air sensitivity.

(h) **$FeCl_2(PPh_3)_2$.** Unsaturated $FeCl_2L_2$ reacts at 25° with I (1:2 mole ratio) to produce $Fe(NO)_2L_2$ (eq 6).

$$FeCl_2L_2 + 2CoNOD_2 + 2L \rightarrow Fe(NO)_2L_2 + 2CoClD_2L \quad (6)$$

$Co(NO)_2ClL$ is also produced in a complicated side reaction between the two products, $Fe(NO)_2L_2$ and II. This was verified independently. It was also shown that $CoNOD_2$ and $CoClD_2L$ do not react to produce $Co(NO)_2ClL$. The fate of the dimethylglyoximate ligand (FeD_2L?) is uncertain, but free dimethylglyoximate was detected.

Equation 6 involves two NO/Cl interchanges. It is therefore natural to contemplate an intermediate mononitrosyl: $FeNOClL_n$. Early in the course of reaction 6, a transient nitrosyl stretch is observed at 1775 cm^{-1}. This compound is stable in the absence of $CoNOD_2$; that is, it does not readily disproportionate to $Fe(NO)_2L_2$ and $FeCl_2L_2$. Only $Fe(NO)_2L_2$ is present 25 min after initiating the reaction of a concentrated solution of $FeCl_2L_2$ with I in a 4:1 mole ratio; therefore, the mononitrosyl must react more rapidly with the transfer reagent (I) than does $FeCl_2L_2$. Similar behavior is observed in transfer to $CoCl_2L_2$ and $CoNOCl_2L_2$. A direct approach at production of $FeNOClL_2$ by NO/Cl redistribution at reflux in THF (eq 7) was fruitless.

$$FeCl_2L_2 + Fe(NO)_2L_2 \rightarrow 2FeNOClL_2 \quad (7)$$

(i) **$FeH(base)(dpe)_2{}^{n+}$.** Because of the variety of known derivatives of $FeH(base)(dpe)_2{}^{n+}$, nitrosyl transfer to this system of compounds is of potential mechanistic significance. $FeHCl(dpe)_2$ is generally unreactive to I in ethanol or THF at 25°. Under reflux in THF, a high yield of $Fe(NO)_2dpe$ is obtained. Coordinative unsaturation at the nitrosyl acceptor may be a prerequisite for successful transfer. For example, chloride dissociation from $FeHCl(dpe)_2$ may occur in THF. To suppress this, the reaction was repeated in refluxing benzene. Again, $Fe(NO)_2dpe$ was produced.

We have measured the conductivity of $FeHCl(dpe)_2$ in purified, degassed acetonitrile at 25°. The compound is initially a nonconductor, but ionic dissociation occurs slowly (~18 h), presumably producing $[FeHCl(dpe)_2(CH_3CN)]Cl$. Attempted nitrosyl transfer to $FeHCl(dpe)_2$ in acetonitrile fails at 25°. Although no iron nitrosyl is produced, the NO stretching frequency of $CoNOD_2$ is altered during the course of the reaction. This is entirely consistent with adduct formation between $CoNOD_2$ and liberated Cl^- to produce $CoNOD_2Cl^-$. Vibrational frequencies of $FeH(dpe)_2(CH_3CN)^+$ are also observed.

All of the above reactions were run with only 1 mol of I per mole of iron. The anticipated product had been $FeNO(dpe)_2{}^+$. In fact, reaction of $FeHCl(dpe)_2$ with I in ethanol in the presence of NH_4PF_6 does produce some $[FeNO(dpe)_2]PF_6$, but the major product remains $Fe(NO)_2dpe$.

In an effort to identify certain potential intermediates in the double nitrosyl transfer which produces $Fe(NO)_2dpe$, two additional transfers were attempted. Under argon, $FeHCl(dpe)_2$ reacts with THF in the presence of $NaBPh_4$ to produce $[FeH(dpe)_2THF]BPh_4$. The coordinated THF is weakly bound, being replaced even by N_2. $[FeH(dpe)_2THF]BPh_4$ reacts with equimolar I at 25° in THF to produce $Fe(NO)_2dpe$ as the only iron nitrosyl. $[FeNO(dpe)_2]^+$, either as the chloride or the hexafluorophosphate salt, reacts only at reflux in THF, again producing $Fe(NO)_2dpe$. This second result bears on the mechanism of the first reaction. Since $FeNO(dpe)_2{}^+$ undergoes nitrosyl transfer only at elevated temperatures, it cannot be an intermediate in the double nitrosyl transfer to $FeH(dpe)_2(THF)^+$. Instead, an intermediate such as $FeHNO(dpe)_2{}^q$ is suggested.

(j) **$FeCl_2(dpe)$.** We find the reaction of anhydrous $FeCl_2$ with 2 mmol of dpe in benzene produces $FeCl_2dpe$, not $FeCl_2(dpe)_2$ as reported.[16] It is to be noted also that reaction of $Fe(C_2H_4)(dpe)_2$ with I_2 produces FeI_2dpe, and not the bis-dpe complex. Likewise, iodine oxidation of $H_2Fe(dpe)_2$ and direct reaction of $FeI_2(H_2O)_n$ with dpe produce FeI_2dpe.[43] Finally, the product of reaction of $FeCl_2$ with dpe in acetone/$CHCl_3$ is reported to be $FeCl_2dpe$.[44]

$FeCl_2dpe$ reacts with I at 25° in the presence of NH_4PF_6. Curiously, the bis-phosphine complex $[FeNO(dpe)_2]PF_6$ is produced in addition to $Fe(NO)_2dpe$, in a mole ratio of 1:2.

(k) **Others.** Equimolar I, PPh_3, and $MCOCl(PPh_3)_2$ (M = Rh, Ir) do not react upon refluxing 6 h in benzene, THF, or toluene. Addition of 20 mol % of $CoD_2 \cdot 2H_2O$ does not alter this result. Finally, since chloride is known to coordinate to I, equimolar $N(n\text{-}Bu)_4Cl$ was added in an attempt to catalyze nitrosyl transfer to $IrCOCl(PPh_3)_2$ in THF at 65°. No such catalysis was observed.

No gold nitrosyls are known, and no copper nitrosyl has been isolated. Reaction of equimolar I, PPh_3, and $AuCl(PPh_3)$ at 25° in THF for 60 h left the reagents unchanged. Similarly $CuCl(PPh_3)_3$ was unaffected by equimolar I in refluxing CH_2Cl_2 for 1.5 h. An attempt (100 h in THF at 25°) to produce $Co(NO)_3$ from $[Co(NO)_2Cl]_2$ and I was also unsuccessful.

Equimolar $RhNOCl_2L_2$, I, and PPh_3 were refluxed for 7 h in benzene in an attempt to produce $Rh(NO)_2ClL_2$, which would probably exist as a salt. Only unreacted starting materials and traces of $Co(NO)_2ClL$ resulted.

Discussion

Nitrosyl transfer, a general term implying only the migration of coordinated NO from one metal to another, is a reaction of some generality. We wish to further categorize nitrosyl transfer according to whether it is (A) simple nitrosyl transfer, eq 8

$$MNO + M' \rightarrow M'NO + M \quad (8)$$

or (B) NO/X interchange, eq 9.

$$MNO + M'X \rightarrow MX + M'NO \quad (9)$$

The ligand X is taken to be a one-electron ligand.[45] We have shown X may be a halogen or hydrogen, but other examples can be envisioned. Both of these reactions bear strong formal resemblance to the well-studied phenomenon of ligand-mediated electron transfer,[1] and much of what is known in that area may hold for nitrosyl transfer. The detailed nature of the migrating species in nitrosyl transfer is unclear. The nitrosyl ligand is variously claimed to be NO^+, NO^-, or neutral NO, and transfer of each of these must be given serious consideration.

Mechanism of Simple NO Transfer. For simple NO transfer, as it occurs in the initial reaction with $CoCl_2L_2$, net migration of neutral NO is demanded by the reaction stoichiometry. However, the redox versatility of the nitrosyl ligand is evident from the reaction of I with $FeNO(dpe)_2{}^+$. Production of $Fe(NO)_2dpe$ unequivocally implicates net transfer of NO^-. Consistent with this, the second product in this reaction is tentatively characterized as the (presumably solvated) cationic cobalt complex $[CoD_2dpe]PF_6$. We feel that a mechanism involving free (solvated) NO and NO^- is unreasonable. $CoNOD_2$ is stable to reflux in THF, and the proton NMR of this compound shows no evidence for dissociation to paramagnetic CoD_2; this latter test is particularly sensitive. Finally, many of the nitrosyl transfer reactions observed here do not occur with free NO.

Ligand-mediated electron transfer is consistent with our observations. This mechanism is favored since it readily accounts for the ability of I to transfer NO and a variable number of electrons (i.e., NO, NO^-). The exact number of electrons transferred will depend on the energy levels of the transition state $M(\mu\text{-}NO)M'$.

Some support for this mechanism comes from the observation that most nitrosyl acceptors react readily at 25° if they are coordinatively unsaturated ($FeCl_2L_2$, $FeCl_2dpe$, $CoCl_2L_2$, $NiCl_2L_2$, $RuCl_2L_3$, $RuHClL_3$, $RuNOClL_2$, RhL_3Cl). The compounds $HRhCOL_3$ and $HRuNOL_3$, ostensibly saturated, both react at 25°. The former is known from solution molecular weight and ^{31}P NMR studies to dissociate phosphine perceptibly at 25°. We have shown, by observing broadening of the ^{31}P NMR of added PPh_3, that $HRuNOL_3$ also dissociates phosphine, although to a very small extent (eq 10).

$$HRuNOL_3 \rightleftarrows HRuNOL_2 + L \qquad (10)$$

Solutions thus contain unsaturated $HRuNOL_2$ which presumably carries the nitrosyl transfer reaction.[46]

The complexes $FeH(B)(dpe)_2{}^+$ (B = Lewis base) constitute a series of substrates useful in probing the requirement of unsaturation. Our results are consistent with formation of a species $Fe(\mu\text{-}NO)Co$ as a prerequisite to NO transfer. When B, above, is Cl^- or CH_3CN, transfer does not occur at 25°. When B is the readily displaceable molecule THF, the reaction proceeds. $FeHCl(dpe)_2$ does react at reflux in ethanol, where halide dissociation is conceivable. In order to suppress ionic dissociation, the reaction was repeated in benzene. Nitrosyl transfer again proceeds, but only at reflux. If this is to fit into the general mechanism suggested here, dissociation of one or both ends of a phosphorus chelate must occur to a kinetically significant extent.

Mechanism of NO/X Interchange. Mechanistic analysis of NO/Cl interchange is more complex. Although $CoClD_2L$ is a characterized product, the interchange could be (1) NO for Cl, (2) NO^+ for Cl^+, or (3) NO^- for Cl^-. Although the bent NO in I has been *called* NO^-, this alone is inadequate support for the third choice. Moreover, a transfer reagent need not contain a bent nitrosyl; the production of $RuNOClL_2$ by eq 11 involves nitrosyl transfer from a nearly linear RuNO group.[47]

$$RuCl_2L_3 + Ru(NO)_2L_2 \rightarrow 2RuNOClL_2 + L \qquad (11)$$

If the interchange were NO^- for Cl^-, the reaction is then best described as a bimolecular substitution reaction (eq 12).

$$CoNOD_2 + MCl \rightarrow D_2Co^+ + MNO + Cl^- \qquad (12)$$

The charge separation required in this mechanism, coupled with the instability of Co(III) without six ligands, would seem to make this a high energy bath. The same problem flaws the NO^+/Cl^+ route, as does the improbability of producing Cl^+. Moreover, this mechanism produces $CoD_2{}^-$, a known reactive species which would certainly attack some of the solvents used here. Thus, interchange of neutral NO and Cl groups seems most plausible.

In the instances of NO/H interchange, choosing from among the three transfers NO^q for H^q ($q = 0, \pm1$) is difficult because the fate of the hydrogen and the cobalt could not be established. By analogy with the chloride reactions, $HCoD_2L$ is assumed to be the product. Our inability to characterize this species is then reasonable in view of the demonstrated instability of this complex.[48]

The NO/H interchanges observed here for $RuHClL_3$ and $RuHCOL_3$ are formally similar to the reactions of these hydrides with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (abbreviated R-N(NO)Me).[49] These generally occur with the stoichiometry shown in eq 13.

$$RN(NO)Me + L_nMH \rightarrow L_{n-1}MNO + RNHMe + L \quad (13)$$

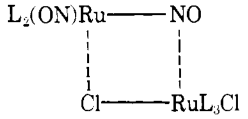
We have shown here that both $CoNOD_2$ and the sulfonamide produce the same products with $HRhCOL_3$. The sulfonamide also reacts with $FeHCl(dpe)_2$ in the presence of $NaBPh_4$ to produce $[FeNO(dpe)_2]BPh_4$.[49] This is only a minor product in the nitrosyl transfer with I, the major product being $Fe(NO)_2dpe$. In order to settle this apparent discrepancy, we have reexamined the sulfonamide/$FeHCl(dpe)_2$ reaction and find that $Fe(NO)_2dpe$ is also produced in small yield. The difference between the two nitrosyl transfer reagents is thus quantitative, not qualitative.

Nitrosyl/halogen or hydrogen interchanges bear a formal resemblance to redistribution reactions of main group elements (eq 14).[50]

$$MR_n + M'R'_m \rightleftarrows MR_{n-q}R'_q + M'R'_{m-q}R_q \qquad (14)$$

Very little mechanistic information is available on these reactions, but some qualitative comparison with NO transfer can be made. If $M = M' = Si$ ($n = m = 4$) uncatalyzed equilibration occurs only very slowly even at elevated temperatures. If M = Al, M′ = Si, alkyl interchange is still very slow. If M = M′ = Al, reorganization is rapid. In this last instance, a four-center $Al(\mu\text{-}R,R')$ Al bridged intermediate is probable, although *ate* complexes of formula M[MRR′] have been proposed.[51] In the aluminum alkyl exchanges, it is known that Al_2R_6 dimers are unreactive to redistribution in comparison to the corresponding monomer, AlR_3. Likewise, Lewis bases slow the exchange by forming saturated $B \rightarrow AlR_3$ species. The one striking similarity between NO/X interchange and classical redistribution is thus the need for coordinative unsaturation.

For NO/Cl interchanges, one additional mechanistic feature requires discussion; the sequence of the migration of the two groups. If two groups are to migrate, it is natural to envision a transition state with both groups bridging the two metals. For the reaction of $Ru(NO)_2L_2$ with $RuCl_2L_3$ (eq 11), this is quite plausible (III).[52] However, for the majority of reactions described here, the rigidly coplanar CoD_2 group makes such a mechanism unlikely. In these instances, simple nitrosyl transfer may occur as a first step to produce the known odd-electron species CoD_2. This readily oxidized species may then undergo reorganization in the solvent cage to abstract a halogen atom from the very unstable cage partner of general formula M(NO)Cl. We have made several attempts to utilize the halogen acceptor capacity of CoD_2 in order to catalyze otherwise sluggish transfers (eq 15, 16).



III

$$CoD_2 + MCl \rightarrow CoD_2Cl + M \qquad (15)$$

$$M + CoNOD_2 \rightarrow MNO + CoD_2 \qquad (16)$$

The results were uniformly negative.

Competing Reactions. A side-reaction observed several times is the production of tetrahedral base adducts of the unit $Co(NO)_2{}^+$. Destruction of the planar CoD_2 unit is indicated and free dimethylglyoxime was detected. While this would seem to indicate that the planar CoD_2 unit is not as stable as generally assumed, we favor an alternative explanation: it is the unit $Co(NO)_2^+$ which is especially stable. This factor may contribute to the reducing ability of NO in reductive nitrosylation.[54] We have noted that solvent oxidation of $CoNO(PPh_3)_3$ in CH_2Cl_2 produces $Co(NO)_2(PPh_3)_2^+$. Finally, $CoNO(SacSac)_2$ spontaneously disproportionates quantitatively to $Co(NO)_2(SacSac)$ and $Co(SacSac)_3$.[55]

A second side-reaction can result in a deviation from the nitrosyl transfer products noted in eq 8 and 9. In the reaction of I with $RuCl_2L_4$ and $RhClL_3$, the halogenated products $RuNOCl_3L_2$ and $RhNOCl_2L_2$ are produced in addition to $RuNOClL_2$ and $RhNOL_3$. In the latter case, it was demonstrated that $RhNOL_3$ is oxidized by $CoClD_2(PPh_3)$ (not generally considered an oxidizing agent!) to produce $RhNOCl_2L_2$. The dinitrosyl $Ru(NO)_2L_2$ was shown to react (eq 5) with $COClD_2(PPh_3)$ to produce $RuNOCl_3L_2$ *and the nitrosyl transfer reagent itself.*

Conclusion

In contemplating nitrosyl transfer as a synthetic tool, it would be useful to be able to predict whether simple NO transfer or NO/X interchange will occur. The following analogy to electron transfer is useful in this regard.

Redox reactions are characterized as complementary or noncomplementary according to whether the oxidant and reductant do or do not transfer the same number of electrons.[1]

$$Cr^{2+} + Co^{3+} \rightarrow Cr^{3+} + Co^{2+} \qquad (17)$$

$$2Cr^{2+} + Tl^{3+} \rightarrow 2Cr^{3+} + Tl^{+} \qquad (18)$$

Reaction 17 is complementary while reaction 18 is not. $CoNOD_2$, if it formally transfers neutral NO,[56] can provide to an acceptor a ligand which donates one or three electrons. Thus $CoNOD_2$ can be said to undergo complementary simple NO transfer to 17-electron and 15-electron complexes. The compounds $CoCl_2L_2$, $NiClL_3$, and $CrCl_6^{3-}$ are nitrosyl acceptors of this type. $V(CO)_6$ and CoD_2 itself are additional examples. Simple NO transfer to a 16-electron complex is a noncomplementary reaction. Just as Cr(IV) (or possibly Tl(II)) is not isolated in eq 18, the initial product of simple NO transfer is not observed in noncomplementary nitrosyl transfers. Subsequent halogen transfer to CoD_2 completes the NO/X interchange and converts a 16-electron complex into an 18-electron complex. Viewed in this way, it is possible to predict whether nitrosyl transfer will occur as simple transfer or NO/X interchange.

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