Halide Nucleophilic Attack on the $[(\eta^5\text{-}C_5R_5)Re(CO)_2(NO)]^+$ Cations: $(\eta^5\text{-}C_5R_5)Re(CO)(NO)X$ and $[fac\text{-}X_3Re(CO)_2(NO)]^-$ Formation through Competitive Loss of CO and $(\eta^5\text{-}C_5R_5)$ (R = H, CH_3)

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Treatment of $[CpRe(CO)_2(NO)][BF_4]$ with 5 equiv of NaI in acetone at room temperature affords a ca. 3:1 mixture of $Na[fac\text{-}I_3Re(CO)_2(NO)]$ and $CpRe(CO)(NO)I$ (Cp = $\eta^5\text{-}C_5H_5$). Using [PPN]Cl in place of NaI results in the formation of a ca. 1:1 mixture of $[PPN][fac\text{-}Cl_3Re(CO)_2(NO)]$ and $CpRe(CO)(NO)Cl$. X-ray structural data for $[PPN][fac\text{-}Cl_3Re(CO)_2(NO)]$, $C_{38}H_{30}N_2O_3P_2Cl_3Re$: monoclinic space group $P2_1/c$, $a = 14.002$ (2) Å, $b = 18.143$ (2) Å, $c = 15.105$ (2) Å, $\beta = 99.75$ (2)°, $Z = 4$, $R/R_w = 6.19/6.01\%$. Anion metathesis occurs when $[Cp^*Re(CO)_2(NO)][BF_4]$ is treated with 1.5 equiv of NaI in acetone, affording crystalline $[Cp^*Re(CO)_2(NO)]I$ in 90% yield ($Cp^* = \eta^5\text{-}C_5Me_5$). The crystal structure of both the BF_4^- and I^- salts are nearly identical, with linear chains of alternating piano stool cations and corresponding anions. X-ray data for $[Cp^*Re(CO)_2(NO)]I$, $C_{12}H_{15}NO_3ReI$: orthorhombic space group *Pbcm*, $a = 10.033$ (5) Å, $b = 12.768$ (3) Å, $c = 12.088$ (4) Å, $Z = 4$, $R/R_w = 2.46/3.65\%$. X-ray data for $[Cp^*Re(CO)_2(NO)][BF_4]$, $C_{12}H_{15}BF_4NO_3Re$: orthorhombic space group *Pbcm*, $a = 10.398$ (3) Å, $b = 12.981$ (3) Å, $c = 12.096$ (3) Å; $Z = 4$, $R/R_w = 3.64/4.69\%$. $Cp^*Re(CO)(NO)I$ is formed in nearly quantitative yield from the solid-state thermolysis of $[Cp^*Re(CO)_2(NO)]I$. X-ray data for $C_{11}H_{15}NO_2ReI$: monoclinic space group $P2_1/n$, $a = 7.364$ (2) Å, $b = 14.602$ (3) Å, $c = 13.038$ (2) Å, $\beta = 91.87$ (2)°, $Z = 4$, $R/R_w = 3.39/4.85\%$. The formation of $Cp^*Re(CO)(NO)Br$ is detected by FT-IR when KBr pellets of $[Cp^*Re(CO)_2(NO)][BF_4]$ are prepared and heated. Treatment of $[Cp^*Re(CO)_2(NO)][BF_4]$ with 5 equiv of [PPN]Cl gives a ca. 4:1 mixture of $[PPN][fac\text{-}Cl_3Re(CO)_2(NO)]$ and $Cp^*Re(CO)(NO)Cl$.

Introduction

Numerous electronic structure studies of the half-sandwich complexes $CpM(CO)_3$ and $CpCr(CO)_2NO$ have addressed the relative donor/acceptor properties of carbonyl and nitrosyl ligands (M = Mn, Re; Cp = $\eta^5\text{-}C_5H_5$).[2] Synthetic studies on related complexes have described carbonyl substitution reactions leading to neutral and cationic $CpM(CO)_2L$ and $CpM(CO)(NO)L$ products (L = PR_3, I^-).[3,4] In 1979, Kolthammer and Legzdins reported that the thermally sensitive $CpMn(CO)(NO)I$ complex can be easily isolated from the treatment of the $[CpMn(CO)_2NO]^+$ cation with I^- at ambient temperature.[4c] The same study showed the third-row congener complex cation $[CpRe(CO)_2(NO)]^+$ to be inert to carbonyl substitution by I^- even under forcing conditions. Although difficult to substitute, a carbonyl ligand of $[CpRe(CO)_2(NO)]^+$ has been transformed in a stepwise fashion to CHO, CH_2OH, and CH_3.[5] More recent work has shown that oxidation of CO to CO_2 by $ONMe_3$ or PhIO is often necessary for inducing CO substitution in the $[CpRe(CO)_2(NO)]^+$ and $[Cp^*Re(CO)_2(NO)]^+$ cases ($Cp^* = \eta^5\text{-}C_5Me_5$).[6] The rather stable $(\eta^5\text{-}C_5R_5)Re(CO)(NO)I$ derivatives are accessible via the treatment of $(\eta^5\text{-}C_5R_5)Re(CO)(NO)CH_3$ complexes with I_2[4c] or HI.[7]

Due to the known difficulty in effecting CO substitution in $[(\eta^5\text{-}C_5R_5)Re(CO)_2(NO)]^+$ cations, the reported formation of $Cp^*Re(CO)(NO)Br$ when $[Cp^*Re(CO)_2(NO)][BF_4]$ is treated with $[n\text{-}Bu_4N]Br$ in boiling dioxane would appear to contradict the inert nature of its Cp analogue.[8] From basic electronic arguments, one might expect the $[Cp^*Re(CO)_2(NO)]^+$ cation to be even less prone to loss of CO than the Cp analogue. Increased Re–CO dπ–pπ back-donation and increased steric demands associated with the Cp* ligand are known to impede associative substitution reactions.[9]

As a result of our interests in the formation and reactivity of organometallic halide complexes,[10] our present reexamination of the reactivity of the $[CpRe(CO)_2(NO)]^+$ and $[Cp^*Re(CO)_2(NO)]^+$ cations with halides shows the $[CpRe(CO)_2(NO)]^+$ cation

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to react with halides faster than $[Cp^*Re(CO)_2(NO)]^+$, leading to CpRe(CO)(NO)X by loss of a CO ligand and $[\textit{fac}\text{-}X_3Re(CO)_2(NO)]^-$ by loss of the $(\eta^5\text{-}C_5R_5)$ ligand. Increased Re–CO thermal stability in the Cp* case permits the characterization of an intermediate $[Cp^*Re(CO)_2(NO)]I$ salt which independently undergoes CO loss at elevated temperatures.

Results

Reaction of $[CpRe(CO)_2(NO)][BF_4]$ with NaI. The addition of 5 equiv of NaI to a room-temperature solution of $[CpRe(CO)_2(NO)][BF_4]$ in acetone-d_6 results in an instantaneous color change from yellow to deep orange (eq 1). The ^{1}H NMR spectrum shows the initial δ 6.66 singlet for the $[CpRe(CO)_2(NO)][BF_4]$ salt to be replaced by the δ 6.11 singlet of CpRe(CO)(NO)I with ca. 30% the intensity of the starting material signal. Also visible in the spectrum are signals corresponding to 9,10-dihydrofulvalene.[11] When a preparative scale reaction in acetone is directly monitored by IR spectroscopy, the initial ν_{CO} bands at 2110 and 2054 cm^{-1} for the $[CpRe(CO)_2(NO)]^+$ cation are completely replaced within 2 min by two strong absorptions at 2074 and 2005 cm^{-1} and a weaker shoulder at 1993 cm^{-1} (the ν_{NO} region is obscured by solvent). Examination of the IR spectrum of the reaction residue as a KBr pellet reveals strong absorptions at 2083, 2015, and 1770 cm^{-1}. Weaker absorptions at 1975 and 1712 cm^{-1} correspond to the ν_{CO} and ν_{NO} bands of CpRe(CO)(NO)I. Elution of the reaction residue on a SiO_2 column with CH_2Cl_2 affords CpRe(CO)(NO)I in 21% yield. Further elution with ethyl acetate produces a yellow zone that affords $Na[\textit{fac}\text{-}I_3Re(CO)_2(NO)]$ in 75% yield.[13]

$$2[CpRe(CO)_2(NO)][BF_4] + 5I^- \xrightarrow{\text{acetone, 20 °C}} CpRe(CO)(NO)I + [\textit{fac}\text{-}I_3Re(CO)_2(NO)]^- + Cp\text{–}Cp \quad (1)$$

When $[CpRe(CO)_2(NO)][BF_4]$ is treated dropwise with 1 equiv of NaI in acetone, the IR spectrum of the ending reaction solution shows strong absorptions of the $[\textit{fac}\text{-}I_3Re(CO)_2(NO)]^-$ anion together with lower intensity absorptions from unreacted starting material and CpRe(CO)(NO)I. A similar reaction in acetone-d_6 monitored by ^{1}H NMR spectroscopy shows a ca. 2:1 ratio of $[CpRe(CO)_2(NO)][BF_4]$ to CpRe(CO)(NO)I.

Reaction of $[CpRe(CO)_2(NO)][BF_4]$ with Cl$^-$. The $[CpRe(CO)_2(NO)][BF_4]$ salt is essentially insoluble in $CDCl_3$, with only the appearance of a very weak singlet at δ 6.40 ppm in the ^{1}H NMR spectrum suggesting its presence in solution.[5e] The addition of 5 equiv of [PPN]Cl to the tube leads to a yellow, homogeneous solution within 5 min. The ^{1}H NMR spectrum shows signals attributable to free 9,10-dihydrofulvalene as well as two singlets at δ 5.82 and 5.79 in a 1:4 intensity ratio, respectively. Over a period of an hour the δ 5.82 signal, corresponding to CpRe(CO)(NO)Cl, grows in at the expense of the signal at δ 5.79 to become the only signal in this region of the spectrum. The identity of the species giving the singlet at δ 5.79 is not known. When a similar preparative scale reaction in CH_2Cl_2 is examined by IR spectroscopy, moderate absorptions due to CpRe(CO)(NO)Cl are clearly visible, but the very strong absorptions at 2090, 2013, and 1765 cm^{-1} indicate the presence of the $[\textit{fac}\text{-}Cl_3Re(CO)_2(NO)]^-$ anion (eq 2): The isolation of pure CpRe(CO)(NO)Cl in 46% yield is possible by extraction of the crude reaction residue with warm toluene. Recrystallization of the remaining residue from CH_2Cl_2/toluene results in the isolation of $[PPN][\textit{fac}\text{-}Cl_3Re(CO)_2(NO)]$ as large yellow needles coated with colorless $[PPN][BF_4]$.

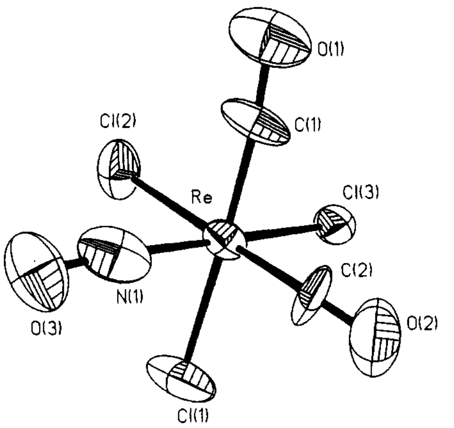

Figure 1. Thermal ellipsoid plot of the $[\textit{fac}\text{-}Cl_3Re(CO)_2(NO)]^-$ anion showing the atom numbering scheme.

$$[CpRe(CO)_2(NO)][BF_4] + 5[PPN]Cl \xrightarrow{CDCl_3} CpRe(CO)(NO)Cl + Cp\text{–}Cp + [PPN][\textit{fac}\text{-}I_3Re(CO)_2(NO)] + [PPN][BF_4] \quad (2)$$

A single-crystal X-ray analysis for $[PPN][\textit{fac}\text{-}Cl_3Re(CO)_2(NO)]$ clearly shows the facial coordination geometry of the $[ReCl_3]$ moiety with a nearly perfect right angle geometry around the Re atom (Figure 1). Crystal data are summarized in Tables I–III. The relatively short Re–Cl(3) distance leads us to conclude that Cl(3) is trans to the nitrosyl ligand. The geometry of the [PPN] cation is unexceptional, with a $\angle P(1)\text{–}N(1)\text{–}P(2)$ of 143.5° and an average P–N distance of 1.57 (1) Å.

Reaction of $[Cp^*Re(CO)_2(NO)][BF_4]$ with I$^-$. The addition of 1.5 equiv of I$^-$ to an acetone solution of $[Cp^*Re(CO)_2(NO)][BF_4]$ results in a rapid color change from bright yellow to red-orange. After the mixture is stirred for 15 min at room temperature, removal of solvent, extraction with CH_2Cl_2, and recrystallization from CH_2Cl_2/toluene produces air stable, orange flake-like crystals of $[Cp^*Re(CO)_2(NO)]I$ in 90% yield (eq 3). Like the BF_4 salt, $[Cp^*Re(CO)_2(NO)]I$ is quite soluble in common polar organic solvents and is insoluble in alkane and aromatic hydrocarbon solvents. The ^{13}C NMR signal for the carbonyl ligands in $[Cp^*Re(CO)_2(NO)]I$ is only slightly shifted from that observed in the BF_4^- salt, and there is only a slight lowering of the ν_{CO} and ν_{NO} IR absorption energies. Molar conductivities of 86.4 (4) Ω^{-1} cm^2 mol^{-1} and 93.3 (5) Ω^{-1} cm^2 mol^{-1} for the I$^-$ and BF_4^- salts are in the range common for 1:1 electrolytes.[14]

$$[Cp^*Re(CO)_2(NO)][BF_4] + NaI \xrightarrow{\text{acetone}} [Cp^*Re(CO)_2(NO)]I + Na[BF_4] \quad (3)$$

The BF_4^-/I^- metathesis can be detected by monitoring the changes in the ^{1}H NMR spectrum as I$^-$ is added to the BF_4^- salt. Titration with $[n\text{-}Bu_4N]I$ in $CDCl_3$ results in the ^{1}H NMR Cp* singlet shifting steadily to a value of 0.08 ppm downfield of its initial position. A solution containing equimolar amounts of $[Cp^*Re(CO)_2(NO)][BF_4]$ and $[Cp^*Re(CO)_2(NO)]I$ in $CDCl_3$

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Table I. Summary of Crystallographic Data for the Re Complexes

	[Cp*Re(CO)$_2$(NO)]I	[Cp*Re(CO)$_2$(NO)][BF$_4$]	[PPN][*fac*-Cl$_3$Re(CO)$_2$(NO)]
empirical formula	$C_{12}H_{15}NO_3ReI$, 534.3	$C_{12}H_{15}BNO_3F_4Re$	$C_{38}H_{30}N_2O_3P_2Cl_2Re$
fw	534.3	494.3	917.1
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	*Pbcm* (No. 57)	*Pbcm* (No. 57)	*P*2$_1$/*c* (No. 14)
a (Å)	10.033 (5)	10.398 (3)	14.002 (2)
b (Å)	12.768 (3)	12.981 (3)	18.143 (2)
c (Å)	12.088 (4)	12.096 (3)	15.105 (2)
β (deg)	90.0	90.0	99.75 (2)
V (Å^3)	1548.4 (9)	1632.8 (8)	3781.8 (8)
Z	4	4	4
T (°C)	−100	24	24
λ (Å)	0.710 73	0.710 73	0.710 73
μ(Mo Kα) (mm^{-1})	9.928	3.795	3.548
ρ_{calc} (g/cm^3)	2.292	2.01	1.611
final *R*,^{a} R_w^{b}	0.0246, 0.0365	0.0364, 0.0469	0.0618, 0.0601

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [PPN][*fac*-Cl$_3$Re(CO)$_2$(NO)]

	x	*y*	*z*	U_{eq}^{a}
Re	6834 (1)	1570 (1)	9021 (1)	57 (1)
Cl(1)	8348 (5)	970 (5)	9537 (5)	137 (4)
Cl(2)	6051 (6)	579 (4)	9660 (4)	106 (3)
Cl(3)	6696 (4)	878 (3)	7628 (3)	73 (3)
P(2)	8821 (3)	−3341 (3)	10500 (3)	36 (2)
P(1)	6873 (3)	−3628 (2)	9402 (3)	31 (2)
C(1)	5651 (19)	1996 (13)	8661 (17)	87 (11)
O(1)	4864 (14)	2228 (11)	8467 (14)	140 (11)
N(1)	6954 (17)	2027 (12)	10183 (18)	113 (12)
O(3)	7094 (17)	2280 (11)	10926 (13)	135 (11)
C(2)	7381 (21)	2329 (17)	8567 (17)	101 (15)
O(2)	7759 (18)	2765 (14)	8244 (13)	175 (14)
N(2)	7833 (10)	−3723 (7)	10103 (9)	33 (6)
C(12)	7148 (8)	−2485 (7)	8246 (8)	59 (6)
C(13)	7137	−1744	7995	82 (8)
C(14)	6651	−1228	8440	71 (7)
C(15)	6178	−1452	9136	98 (8)
C(16)	6190	−2192	9387	58 (6)
C(11)	6675	−2708	8942	33 (4)
C(42)	8822 (14)	−4352 (12)	11876 (13)	60 (6)
C(43)	9149 (15)	−4638 (12)	12728 (13)	64 (6)
C(44)	9858 (16)	−4278 (12)	13287 (14)	66 (7)
C(45)	10280 (15)	−3657 (11)	13055 (14)	68 (7)
C(46)	9926 (14)	−3320 (11)	12197 (12)	55 (6)
C(41)	9221 (12)	−3729 (9)	11608 (11)	34 (5)
C(32)	7707 (13)	−4707 (10)	8468 (11)	41 (5)
C(33)	7695 (14)	−5200 (11)	7767 (13)	58 (6)
C(34)	6928 (14)	−5284 (10)	7128 (12)	48 (5)
C(35)	6136 (14)	−4855 (11)	7121 (12)	53 (6)
C(36)	6097 (14)	−4316 (10)	7790 (12)	47 (5)
C(31)	6907 (13)	−4276 (9)	8491 (11)	34 (5)
C(22)	4914 (17)	−3728 (11)	9502 (13)	70 (7)
C(23)	4125 (16)	−3903 (12)	9906 (15)	70 (7)
C(24)	4294 (15)	−4146 (11)	10756 (14)	60 (6)
C(25)	5199 (16)	−4277 (11)	11184 (13)	66 (7)
C(26)	6020 (14)	−4109 (11)	10803 (13)	55 (6)
C(21)	5857 (12)	−3827 (9)	9937 (11)	29 (5)
C(52)	9306 (8)	−1851 (8)	10348 (8)	92 (8)
C(53)	9158	−1102	10482	134 (11)
C(54)	8416	−874	10929	85 (8)
C(55)	7821	−1395	11243	95 (8)
C(56)	7969	−2145	11108	68 (7)
C(51)	8711	−2372	10661	36 (5)
C(62)	10594 (19)	−3789 (13)	10181 (15)	88 (8)
C(63)	11319 (20)	−3936 (14)	9640 (18)	102 (9)
C(64)	11145 (18)	−3701 (12)	8758 (16)	79 (8)
C(65)	10330 (17)	−3451 (14)	8411 (14)	80 (7)
C(66)	9609 (15)	−3322 (13)	8945 (14)	73 (6)
C(61)	9754 (11)	−3487 (10)	9838 (10)	35 (5)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

gives a single sharp Cp* resonance midway between the resonances of the pure salts, indicating that fast anion exchange occurs at room temperature.

Table III. Selected Bond Lengths and Bond Angles for [PPN][*fac*-Cl$_3$Re(CO)$_2$(NO)]

	Bond Lengths (Å)		
Re–Cl(1)	2.393 (7)	P(2)–N(2)	1.573 (13)
Re–Cl(2)	2.394 (7)	P(1)–N(2)	1.573 (13)
Re–Cl(3)	2.430 (6)	C(1)–O(1)	1.170 (32)
Re–C(1)	1.825 (25)	C(2)–O(2)	1.110 (40)
Re–C(2)	1.768 (31)	N(1)–O(3)	1.197 (32)
Re–N(1)	1.922 (26)		
	Bond Angles (deg)		
Cl(1)–Re–Cl(2)	88.2 (3)	Cl(1)–Re–C(2)	93.6 (9)
Cl(1)–Re–Cl(3)	89.0 (2)	Cl(2)–Re–C(2)	177.6 (10)
Cl(2)–Re–Cl(3)	89.2 (2)	Cl(3)–Re–C(2)	92.4 (9)
Cl(1)–Re–C(1)	177.2 (8)	C(1)–Re–C(2)	89.2 (12)
Cl(2)–Re–C(1)	89.1 (8)	N(1)–Re–C(2)	92.4 (11)
Cl(3)–Re–C(1)	91.4 (8)	Re–C(1)–O(1)	174.8 (23)
Cl(1)–Re–N(1)	87.9 (7)	Re–N(1)–O(3)	174.8 (20)
Cl(2)–Re–N(1)	86.0 (7)	Re–C(2)–O(2)	174.3 (28)
Cl(3)–Re–N(1)	174.4 (7)	P(2)–N(2)–P(1)	143.5 (9)
C(1)–Re–N(1)	91.4 (10)		

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [Cp*Re(CO)$_2$(NO)]I

	x	*y*	*z*	U_{eq}^{a}
Re	1196 (1)	4680 (1)	2500	29 (1)
I	−3192 (1)	4455 (1)	2500	35 (1)
C(1)	3190 (7)	3807 (5)	2500	30 (2)
C(2)	3162 (5)	4465 (3)	1546 (4)	27 (1)
C(3)	3072 (5)	5526 (3)	1899 (4)	26 (1)
C(4)	3413 (8)	2647 (6)	2500	38 (2)
C(5)	3307 (7)	4099 (5)	372 (5)	47 (2)
C(6)	3142 (6)	6476 (4)	1172 (5)	39 (2)
N	144 (9)	5917 (7)	2500	84 (4)
O(1)	−395 (8)	6708 (6)	2500	125 (5)
C(7)	234 (5)	4035 (5)	1341 (5)	46 (2)
O(2)	−263 (5)	3644 (6)	607 (5)	96 (3)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

The results of the single-crystal X-ray analyses for [Cp*Re(CO)$_2$(NO)]I and [Cp*Re(CO)$_2$(NO)][BF$_4$] show the two salts to be isomorphous. The crystal data are summarized in Tables III–V.[15] The Re atoms and the anions lie on a crystallographic mirror plane, producing linear chains of alternating cations and anions along the *a* crystallographic axis (Figure 2). The length of the *a* axis is the distance between the Re atoms. Thus, the approximate 4% elongation of *a* in the BF$_4^-$ salt corresponds to the slightly larger size of the BF$_4^-$ ion compared to the I$^-$ ion. The rather well-behaved geometry of the BF$_4^-$ ion may possibly be attributed to weak hydrogen bonding interactions with the CH$_3$ groups on the Cp* ligand (average F–C distance is 3.68 Å). The apical F atom of the BF$_4^-$ ion is 3.57 Å from the Re atom of the

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(15) The coordinates of the atoms in both structures have been transformed such that the values in Tables IV and V reflect the isomorphism of the two crystals.

Table V. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Cp^*Re(CO)_2(NO)][BF_4]$

	x	*y*	*z*	U_{eq}[a]
Re	1216 (1)	4706 (1)	2500	49 (1)
N	231 (15)	5897 (21)	2500	127 (10)
O(1)	−336 (17)	6719 (13)	2500	187 (14)
C(7)	261 (10)	4068 (12)	1365 (11)	75 (5)
O(2)	−202 (11)	3673 (12)	627 (12)	154 (7)
C(1)	3095 (14)	3832 (11)	2500	52 (5)
C(2)	3073 (11)	4496 (8)	1540 (9)	52 (3)
C(3)	3004 (10)	5533 (7)	1911 (9)	48 (3)
C(4)	3298 (18)	2687 (13)	2500	87 (8)
C(5)	3266 (15)	4126 (12)	370 (11)	101 (6)
C(6)	3119 (13)	6451 (9)	1199 (10)	79 (5)
B	−3375 (14)	4519 (12)	2500	155 (22)
F(1)	−3941 (22)	5358 (10)	2500	208 (15)
F(2)	−2208 (11)	4683 (24)	2500	425 (34)
F(3)	−3678 (16)	4017 (10)	1660 (10)	208 (8)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

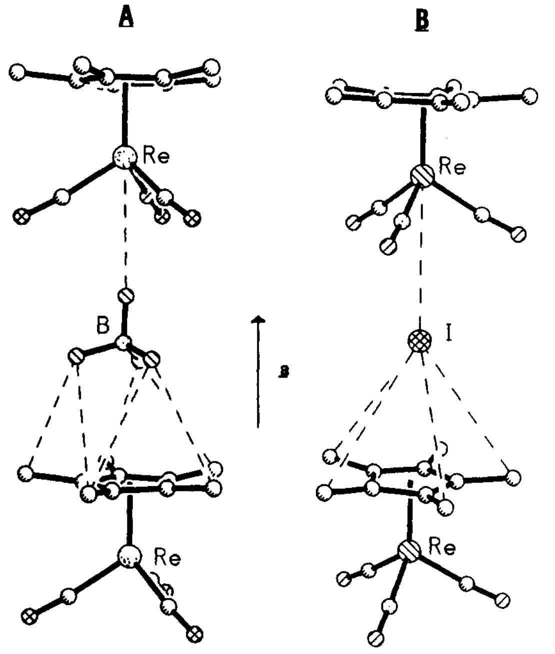

Figure 2. Section of the linear anion/cation packing along the *a* axis in $[Cp^*Re(CO)_2(NO)[BF_4]$ (A) and $[Cp^*Re(CO)_2(NO)]I$ (B).

adjacent cation. In the I^- salt, the I^- ion is 4.41 Å from the Re atom in the adjacent cation and an average of 4.40 Å from the carbon atoms of the nearby Cp* methyl groups.

Within the error limits of the data, the geometries of the $[Cp^*Re(CO)_2(NO)]^+$ cations are identical in the two crystals. A thermal ellipsoid plot of the $[Cp^*Re(CO)_2(NO)]^+$ cation from the $[Cp^*Re(CO)_2(NO)]I$ salt is shown in Figure 3. Similar to the situation in numerous other complexes containing the [Cp*Re] fragment,[16] the Cp* ligand is bound to the Re atom in a symmetrical fashion, with a $Re\text{–}Cp^*_{centroid}$ distance of 1.94 Å. The choice of NO as the ligand in the crystallographic mirror plane is consistent with the expected C_s molecular symmetry. However, the similarity between the Re–CO and Re–NO geometries does not permit unambiguous discrimination between NO and CO.

Thermolysis of $[Cp^*Re(CO)_2(NO)]I$. Heating crystalline $[Cp^*Re(CO)_2(NO)]I$ to 110 °C causes the material to turn dark red and melt with vigorous gas evolution. The residual solid is found to be spectroscopically pure $Cp^*Re(CO)(NO)I$ (eq 4). IR

$$[Cp^*Re(CO)_2(NO)]I \xrightarrow{\Delta} \underset{99\%}{Cp^*Re(CO)(NO)I} + CO \quad (4)$$

spectroscopy indicates that carbon monoxide is the only volatile

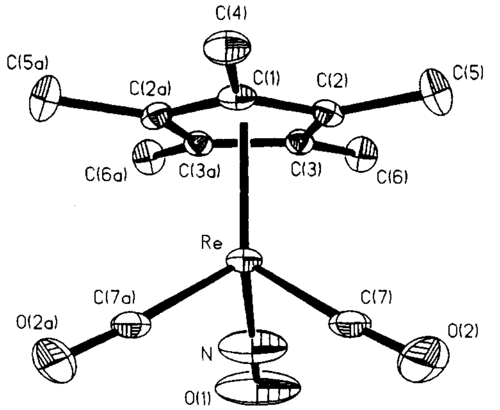

Figure 3. Thermal ellipsoid plot of the $[Cp^*Re(CO)_2(NO)]^+$ cation from the BF_4^- salt.

product in the head-space gas above the thermolysis reaction. The mass spectrum of solid $[Cp^*Re(CO)_2(NO)]I$ obtained by direct insertion on a heated inlet probe is identical to the spectrum of authentic $Cp^*Re(CO)(NO)I$. Thermolysis of $[Cp^*Re(CO)_2(NO)]I$ in boiling dioxane also leads to the recovery of $Cp^*Re(CO)(NO)I$ in virtually quantitative yield.[17] Only when $[Cp^*Re(CO)_2(NO)]I$ is treated with a large excess of $[n\text{-}Bu_4N]I$ in refluxing dioxane do we observe traces of the $[fac\text{-}I_3Re(CO)_2(NO)]^-$ anion in the reaction residue by IR spectroscopy.

Attempts to prepare KBr pellets of $[Cp^*Re(CO)_2(NO)]I$ for IR analysis result in partial conversion to $Cp^*Re(CO)(NO)I$ as detected by solid-state IR spectroscopy. Examination of a $CDCl_3$ extract of the pellet by ^1H NMR spectroscopy also indicates the presence of a small amount of $Cp^*Re(CO)(NO)Br$ (δ 2.07).[7] Heating the pellet to 150 °C for 30 s causes the complete conversion of any remaining $[Cp^*Re(CO)_2(NO)]I$ to $Cp^*Re(CO)(NO)I$ and $Cp^*Re(CO)(NO)Br$ (Figure 4).

Reaction of $[Cp^*Re(CO)_2(NO)][BF_4]$ with Br^- or Cl^-. Repeating the procedure reported by Weber and co-workers,[8] the treatment of $[Cp^*Re(CO)_2(NO)][BF_4]$ with $[n\text{-}Bu_4N]Br$ in refluxing dioxane leads to the disappearance of the starting material after 1 h with the formation of $Cp^*Re(CO)(NO)Br$ together with small amounts of $[n\text{-}Bu_4N][fac\text{-}Br_3Re(CO)_2(NO)]$ (eq 5).

$$[Cp^*Re(CO)_2(NO)][BF_4] + [n\text{-}Bu_4N]Br \xrightarrow{\text{dioxane, }\Delta} Cp^*Re(CO)(NO)Br + [n\text{-}Bu_4N][fac\text{-}Br_3Re(CO)_2(NO)] \quad (5)$$

$Cp^*Re(CO)(NO)Br$ formation is detectable when $[Cp^*Re(CO)_2(NO)][BF_4]$ is ground and heated as a KBr mull.

Treatment of $[Cp^*Re(CO)_2(NO)][BF_4]$ with 5 equiv of [PPN]Cl in 50 °C acetone results in the formation of $Cp^*Re(CO)(NO)Cl$ and $[PPN][fac\text{-}Cl_3Re(CO)_2(NO)]$ (eq 6).

$$[Cp^*Re(CO)_2(NO)][BF_4] + \text{excess }[PPN]Cl \xrightarrow{\text{acetone, }\Delta} [PPN][fac\text{-}Cl_3Re(CO)_2(NO)] + Cp^*Re(CO)(NO)Cl \quad (6)$$

$Cp^*Re(CO)(NO)Cl$ is isolated in ca. 20% yield by a simple extraction of the reaction residue with toluene. Recrystallization of the remaining residue from CH_2Cl_2/toluene affords a

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(16) (a) For a summary of the structures of several Cp^*ReL_n complexes see: Herrmann, W. A.; Herdtweck, E.; Floel, M.; Kulpe, J.; Kusthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165–1182 and references therein. (b) X-ray structure of $CpRe(CO)_3$: Fitzpatrick, P. J.; LePage, Y.; Butler, I. S. *Acta Crystallogr. Sect. B* **1981**, *37*, 1052. Harison, W.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1972**, 678.

(17) X-ray data for $Cp^*Re(CO)(NO)I$ ($C_{11}H_{15}NO_2ReI$): monoclinic space group $P2_1/n$, $a = 7.364$ (2) Å, $b = 14.602$ (3) Å, $c = 13.038$ (2) Å, $\beta = 91.87$ (2)°, $V = 1401.2$ (5) $Å^3$, $Z = 4$, $\rho = 10.863$ mm^{-1}, $R/R_w = 3.39/4.85\%$ for 145 parameters and 1821 data ($F > 6\sigma(F)$), goodness-of-fit = 0.70.

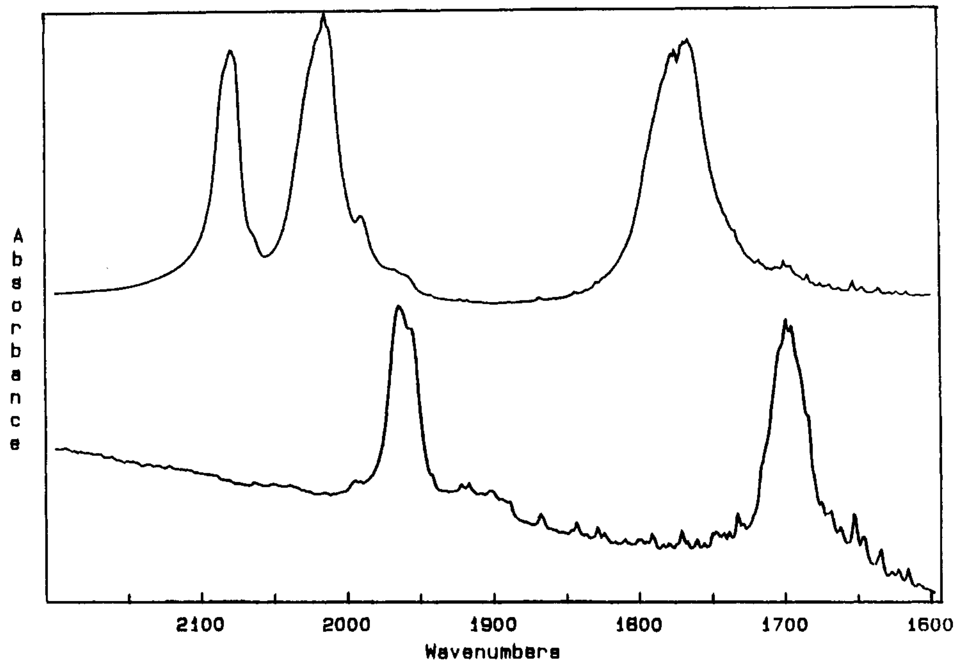

Figure 4. KBr IR spectrum of [Cp*Re(CO)$_2$(NO)]I (upper trace); IR spectrum of the same pellet after heating to 150 °C for 30 s (lower trace).

Table VI. Selected Bond Lengths and Bond Angles for [Cp*Re(CO)$_2$(NO)]I and [Cp*Re(CO)$_2$(NO)][BF$_4$]

[Cp*Re(CO)$_2$(NO)]I		[Cp*Re(CO)$_2$(NO)][BF$_4$]	
	Bond Distances (Å)		
Re–C(1)	2.290 (7)	Re–C(1)	2.26 (1)
Re–C(2)	2.301 (5)	Re–C(2)	2.27 (1)
Re–C(3)	2.288 (5)	Re–C(3)	2.26 (1)
Re–N	1.900 (9)	Re–N	1.85 (2)
Re–C(7)	1.890 (6)	Re–C(7)	1.89 (1)
N–O(1)	1.146 (12)	N–O(1)	1.22 (3)
C(7)–O(2)	1.133 (8)	C(7)–O(2)	1.13 (2)
	Bond Angles (deg)		
Re–N–O(1)	174.4 (8)	Re–N–O(1)	175.0 (17)
Re–C(7)–O(2)	175.2 (5)	Re–C(7)–O(2)	173.9 (11)
N–Re–C(7)	94.5 (3)	N–Re–C(7)	94.4 (6)
C(7)–Re–C(7A)	95.6 (4)	C(7)–Re–C(7A)	93.7 (8)
Cp*$_{cent}$–Re–(C7)	122.2	Cp*$_{cent}$–Re–C(7)	123.1
Cp*$_{cent}$–Re–N	120.8	Cp*$_{cent}$–Re–N	121.0

mixture of [PPN][*fac*-Cl$_3$Re(CO)$_2$(NO)] and traces of residual [PPN] salts.

Discussion

Our results show that CO substitution is a facile process when solutions of [CpRe(CO)$_2$(NO)][BF$_4$] are treated with halides at ambient temperature. We speculate that previous reports indicating no reaction to occur under these conditions to be the result of the similarity of the IR spectra of the starting [CpRe(CO)$_2$(NO)]$^+$ cation and the [*fac*-I$_3$Re(CO)$_2$(NO)]$^-$ anion. It is interesting that the formal replacement of the Cp ligand by three I$^-$ ligands results in such a small shift in the IR bands. One might anticipate the IR absorptions of the formal d^6 [Re(CO)$_2$(NO)] group in the cation to fall at higher energy than those in the anionic complex. However, the rather different ligating properties of the Cp ligand and the I$^-$ ligands apparently balance against the charge effects, resulting in a relatively small shift between the two complexes. Interestingly, the rather protracted reaction time reported for the preparation of Cp*Re(CO)(NO)Br (3 days) is very likely the result of mistaking the IR signals from the [*fac*-Br$_3$Re(CO)$_2$(NO)]$^-$ anion with those from the starting cation.[8]

In contrast to its Cp analogue, only BF$_4^-$/I$^-$ metathesis occurs when [Cp*Re(CO)$_2$(NO)][BF$_4$] is treated with NaI in room-temperature acetone. The fact that CO loss from [Cp*Re(CO)$_2$(NO)I is only observed at elevated temperatures is consistent with our expectation that the difficulty of thermal CO substitution should increase when Cp is replaced with Cp*. The observation of spectral changes when solutions of [Cp*Re(CO)$_2$(NO)][BF$_4$] are treated with Br$^-$ or Cl$^-$ leads us to suspect significant anion metathesis occurs in these cases, too. The detection of a transient ^{1}H NMR signal at δ 5.79 ppm when [CpRe(CO)$_2$(NO)][BF$_4$] is treated with [PPN]Cl may be evidence of anion metathesis in the Cp case. However, the rapid substitution reactivity under ambient temperature conditions precludes the isolation of the new Cl$^-$ salt.

The loss of Cp as 9,10-dihydrofulvalene when the [CpRe(CO)$_2$(NO)]$^+$ cation is attacked by halides suggests the possibility that electron transfer leads to the formation of the 19-electron radical [CpRe(CO)$_2$(NO)].[18] Formal occupation of the e$_g$* (σ-antibonding) level in a 19-electron species would facilitate ligand dissociation. In CpM–NO complexes, such a species may stabilized by Cp "slippage" or M–NO bending.[19] Our observation that I$^-$ is more effective than Cl$^-$ in displacing the Cp ligand of the [CpRe(CO)$_2$(NO)]$^+$ cation would be consistent with the higher reducing power and nucleophilicity of I$^-$ versus Cl$^-$. Even under limiting I$^-$ concentration, we observe predominantly loss of the Cp ligand.

The resistance of the [Cp*Re(CO)$_2$(NO)]$^+$ cation to lose the Cp* ligand is evidence of the Cp* ligand being more firmly bound to Re than the Cp ligand. It may also be an indication that halide nucleophilicity is more important than electron transfer since formation of a 19-electron radical in the more electron rich [Cp*Re(CO)$_2$(NO)]$^+$ cation would be expected to be more difficult by 0.15–0.20 V.[20] Thus, CO loss to give exclusive formation of Cp*Re(CO)(NO)I may follow from irreversible CO loss in a formal 20-electron "[CpRe(CO)$_2$(NO)(I)]" transition state possessing a bent NO ligand or a "slipped" Cp* ligand. The formation of the [*fac*-Cl$_3$Re(CO)$_2$(NO)]$^-$ anion as the major product when [Cp*Re(CO)$_2$(NO)]$^+$ is treated with Cl$^-$ suggests that greater Cp* slippage may occur in an activated [Cp*Re-

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(18) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325.

(19) For a review of Cp ligand slippage see: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(20) (a) Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493. (b) Tilset, M. *J. Am. Chem. Soc.* **1992**, *114*, 2740.

$(CO)_2(NO)]^+/Cl^-$ ion pair, leading to greater Cp* loss.[21] The less nucleophilic Cl^- ion would be expected to be less effective at displacing a CO ligand. Unfortunately, we have not been able to determine the fate of the displaced Cp* ligand.

Experimental Section

Standard Schlenk techniques were employed in all syntheses. Reagent grade solvents were purified by distillation from appropriate drying agents and stored under nitrogen until use. Anhydrous KBr, NaI, $[n\text{-}Bu_4I]I$, $[n\text{-}Bu_4N]Br$, and [PPN]Cl ($Ph_3P{=}N{=}PPh_3{}^+Cl^-$) were obtained from Aldrich. $[CpRe(CO)_2(NO)][BF_4]$[6a] $[Cp^*Re(CO)_2(NO)][BF_4]$[6c] were prepared by literature methods. Routine filtrations were performed through Analytical Filter Pulp (Schleicher and Schuell). Infrared spectra were recorded on a Mattson Polaris-Icon FT spectrometer. Solution spectra were obtained in 0.1 mm NaCl cells and the solvent background was computer subtracted. Solid-state IR spectra were obtained as KBr pellets (prepared at ca. 10 tons of pressure) or as evaporated thin films. Routine NMR data were measured in 5-mm tubes using either a GSX 270 JEOL or a Varian XL300 spectrometer at their respective fields (^1H, 270 or 300 MHz; ^{13}C, 68.9 or 75.4 MHz). ^{31}P NMR spectra were measured on the Varian XL300 spectrometer at 121.4 MHz and referenced to external 85% H_3PO_4. Otherwise, residual solvent peaks were used as internal standards ($CDCl_3$, δ 7.24 [^1H], δ 77.0 [^{13}C]; C_6D_6, δ 7.15 [^1H], δ 128.0 [^{13}C]; acetone-d_6, δ 2.04 [^1H], 29.8 [^{13}C]). Mass spectra were measured with a LKB 2091 mass spectrometer using electron impact ionization and a heated direct inlet probe. Conductance measurements were measured on a YSI Model 31A conductivity bridge (1.0×10^{-3} M solutions in nitromethane, solvent conductivity $\geq 10^{-6}\ \Omega^{-1}\ cm^{-1}$). Melting points were measured with a Mel-Temp device (Laboratory Devices) in open capillaries and are uncorrected. Combustion analyses were carried out by Atlantic Microlabs, Norcross, GA.

Reaction of $[CpRe(CO)_2(NO)][BF_4]$ with I^-. A Schlenk flask was charged with 0.10 g (0.24 mmol) of $[CpRe(CO)_2(NO)][BF_4]$, 0.18 g (1.2 mmol) of NaI, 10 mL of acetone, and a stir bar. The mixture was stirred at room temperature for 15 min and the acetone was removed in vacuo. The residue was extracted with 5 mL of CH_2Cl_2 and transferred to the top of a 0.5×5 cm SiO_2 column prepared in CH_2Cl_2. Elution with CH_2Cl_2 produced a red zone that afforded 0.022 g (0.05 mmol, 21%) of CpRe(CO)(NO)I after removal of solvent. Further elution with ethyl acetate produced a yellow zone that afforded 0.12 g (0.18 mmol, 75%) of Na[*fac*-$I_3Re(CO)_2(NO)$]. IR (cm^{-1}, KBr): ν_{CO}, 2083 (vs), 2012 (vs); ν_{NO}, 1771 (vs). Anal. Calcd for $C_2NO_3NaI_3Re$: C, 3.55; N, 2.07. Found: C, 3.43; N, 1.98.

Synthesis of [PPN][*fac*-$Cl_3Re(CO)_2(NO)$]. Method A. A Schlenk flask was charged with 0.10 g (0.24 mmol) of $[CpRe(CO)_2(NO)][BF_4]$, 0.68 g (1.2 mmol) of [PPN]Cl, 20 mL of CH_2Cl_2, and a stir bar. After the mixture was stirred for 30 min at room temperature, 20 mL of toluene was added to the flask and the volume was reduced in vacuo to the point where crystals appeared. Isolation and evaporation of the toluene solution afforded 0.38 g (0.11 mmol, 46% yield) of CpRe(CO)(NO)Cl. The toluene-insoluble material was dissolved in 10 mL of CH_2Cl_2, and 50 mL of Et_2O was added to precipitate colorless [PPN] salts. Concentration of the filtrate to 10 mL followed by layering with 40 mL of toluene produced yellow needles of [PPN][*fac*-$Cl_3Re(CO)_2(NO)$] that were contaminated with residual colorless [PPN] salts.

Method B. A Schlenk tube was charged with 0.40 g (0.81 mmol) of $[Cp^*Re(CO)_2(NO)][BF_4]$, 2.3 g (4.1 mmol) of [PPN]Cl, and a stir bar. Acetone (50 mL) was added, and the solution was stirred at 50 °C for 2 h. The solvent was concentrated in vacuo to ca. 5 mL, and 15 mL of toluene was added to precipitate the ionic components. Isolation and evaporation of the filtered toluene extract lead to the recovery of Cp*Re(CO)(NO)Cl (0.067 g, 0.16 mmol, 20% yield). The toluene-insoluble residue was redissolved in 20 mL of CH_2Cl_2 and 50 mL of Et_2O was added to precipitate a large portion of the remaining [PPN]Cl and $[PPN][BF_4]$ salts. The supernatant was collected by filtration and concentrated in vacuo to ca. 10 mL. Layering with 30 mL of toluene produced, after the mixture was allowed to stand at room temperature for 2 days, 0.60 g of solid material containing large yellow needles of [PPN][*fac*-$Cl_3Re(CO)_2(NO)$] together with considerable amounts of colorless [PPN] salts. Repeated recrystallizations failed to completely remove the [PPN] salt contaminants. ^1H NMR ($CDCl_3$): δ 7.38–7.66 ($Ph_3P{=}N{=}PPh_3$). ^{13}C NMR ($CDCl_3$): δ 185.8 (*C*O), 126.2–133.9 (resonances of the $[PPN]^+$ cation. ^{31}P NMR ($CDCl_3$): δ 20.48 ($Ph_3P{=}N{=}PPh_3$). IR (KBr): ν_{CO}, 2083, 2006 cm^{-1}; ν_{NO}, 1751 cm^{-1}. Anal. Calcd for $C_{38}H_{30}N_2O_3P_2Cl_3Re$: C, 49.76; H, 3.30; N, 3.05. Found: C, 52.65; H, 3.71; N, 2.90. Mp: 144–146 °C dec.

Synthesis of $[Cp^*Re(CO)_2(NO)]I$. A solution of 0.61 g (1.2 mmol) of $[Cp^*Re(CO)_2(NO)][BF_4]$ in 40 mL of acetone was treated with 0.28 g (1.8 mmol) of NaI, producing a color change from bright yellow to dark orange-red. As monitored by thin film IR spectroscopy, the starting material ν_{CO} and ν_{NO} bands were distinctly shifted by 7–9 cm^{-1} to lower energy. The ^1H NMR spectrum of an aliquot taken to dryness and redissolved in $CDCl_3$ showed a single resonance at δ 2.46 ppm. After 0.5 h the solvent was removed in vacuo and the orange residue was extracted into 40 mL of CH_2Cl_2. Reduction of the filtrate volume to 5 mL followed by addition of 10 mL of toluene produced 0.60 g (0.11 mmol, 92%) of $[Cp^*Re(CO)_2(NO)]I$ as bright orange flakelike crystals after storing at –40 °C for 1 h. ^1H NMR ($CDCl_3$): δ 2.46 (15H, Cp*). ^1H NMR (acetone-d_6): δ 2.58. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 185.6 (CO), 108.3 (C_5Me$_5$), 11.3 (C$_5$*Me*$_5$). ^{13}C NMR (acetone-d_6): δ 187.5 (CO), 109.3 (C_5Me$_5$), 10.7 (C$_5$*Me*$_5$). IR (CH_2Cl_2, cm^{-1}): ν_{CO}, 2090, 2037; ν_{NO}, 1796. IR (acetone, cm^{-1}): ν_{CO}, 2094 (vs), 2037 (vs) (ν_{NO} obscured by solvent absorption). IR (thin film, cm^{-1}): ν_{CO}, 2075 (vs), 2016 (vs); ν_{NO}, 1767 (vs). Mp: 108–110 °C dec. Molar conductivity in nitromethane: $\Lambda_M = 86.4\ (4)\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{12}H_5NO_3ReI$: C, 26.97; H, 2.83; N, 2.62. Found: C, 27.04; H, 2.85; N, 2.59. MS (^{187}Re): [M$^+$], *m/e* 535 (not seen); [M – CO], *m/e* 507 (64%); [M – 2CO], *m/e* 479 (91%); [M – 2CO – NO], *m/e* 449 (100%).

Thermolysis of $[Cp^*Re(CO)_2(NO)]I$. $[Cp^*Re(CO)_2(NO)]I$ (0.30 g, 0.56 mmol) was dissolved in 20 mL of DME and heated at 130 °C for 0.5 h. The solvent was removed in vacuo, resulting in 0.28 g (0.55 mmol, 99%) of a dark red solid identified as Cp*Re(CO)(NO)I by its spectral properties[7] and by X-ray diffraction methods.[17]

An infrared spectral analysis of the volatile byproducts of this reaction was obtained by heating ca. 0.01 g of $[Cp^*Re(CO)_2(NO)]I$ in a 5-mL Ŧ 14/20 flask attached to the side of a 10 cm × 2.5 cm gas cell equipped with a matching Ŧ 14/20 joint and a stopcock. The entire apparatus was evacuated and the attached 5-mL flask was heated until the material decomposed. The cell was then placed in the IR spectrometer for the measurement of the spectrum. The residual solid was examined by IR and NMR spectroscopy.

X-ray Structure of $[Cp^*Re(CO)_2(NO)]I$. A suitably sized crystal was obtained by evaporation from a solution of $[Cp^*Re(CO)_2(NO)]I$ in ethanol. The crystal was mounted in a 0.3-mm diameter X-ray capillary and centered optically on a Siemens P4 diffractometer equipped with an LT-2a low-temperature device that maintained the crystal at –100 °C throughout data collection. Autocentering of 25 reflections gave a primitive orthorhombic cell. Axial photographs confirmed symmetry along all three axes. Analysis of the systematic absences in the data indicated the space group *Pbcm* and the structure was solved using direct methods. The Re, I, C(1), C(4), N, and O(1) atoms were found to lie on a crystallographic mirror plane. The location and anisotropic refinement of all the non-hydrogen atoms in the complex (H atoms refined isotropically) was accomplished by application of the SHELXTL PLUS package of programs.

X-ray Structure of $[Cp^*Re(CO)_2(NO)][BF_4]$. A suitable crystal was selected and mounted vertically on a glass fiber with epoxy cement. The crystal was optically centered on a Nicolet R3m/V diffractometer. The indexing of 25 centered reflections indicated a primitive orthorhombic cell. Axial photographs confirmed the presence of symmetry along all three axes. Systematic absences in the data indicated the space group *Pbcm*. The structure solution (by direct methods) and subsequent anisotropic refinement of non-hydrogen atoms utilized SHELXTL PLUS package of programs. The Re, C(1), C(4), N, O(1), B(1), F(1), and (F2) atoms were found to lie on a crystallographic mirror plane. Hydrogen atoms were generated in idealized positions with fixed thermal parameters (0.08).

X-ray Structure of [PPN][*fac*-$Cl_3Re(CO)_2(NO)$]. A suitably sized crystal was mounted vertically in a 0.3-mm-diameter X-ray capillary and centered optically on a Siemens P4 auto-diffractometer at room temperature. The centering of 25 randomly selected reflections gave a monoclinic cell and an axial photograph revealed symmetry along the *b* axis. Systematic absences in the data set led to the unambiguous selection of the space group $P2_1/c$. The Re atom was located by Patterson methods and the remaining non-hydrogen atoms were located by subsequent difference maps. Due to the limited amount of data, the phenyl ring carbon atoms of the [PPN] ion were refined as rigid groups (including

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(21) A case has recently been made that Cp* ligands slip more easily than Cp ligands: Chetcuti, M. J.; DeLiberato, L. A.; Fanwick, P. E.; Grant, B. E. *Inorg. Chem.* **1990**, *29*, 1295.

riding H atoms). All other non-hydrogen atoms were refined anisotropically. The solution and refinement procedures used the SHELXTL package of programs (Siemens Corp., Madison WI).

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Supplementary Material Available: Tables giving complete details of the X-ray data collection and refinement and complete lists of bond angles, bond distances, final anisotropic thermal parameters, calculated (or refined) H atom coordinates for [Cp*Re(CO)$_2$(NO)]I, [Cp*Re(CO)$_2$(NO)][BF$_4$], [PPN][*fac*-Cl$_3$Re(CO)$_2$(NO)], and Cp*Re(CO)(NO)I and tables of atomic coordinates and equivalent isotropic thermal parameters for the latter three complexes (18 pages). Ordering information is given on any current masthead page.

Registry No. CpRe(CO)(NO)I, 75847-54-0; Na[*fac*-I$_3$Re(CO)$_2$(NO)], 143294-52-4; CpRe(CO)(NO)Cl, 84947-96-6; [PPN][*fac*-Cl$_3$Re(CO)$_2$(NO)], 143294-54-6; Cp*Re(CO)(NO)Cl, 133670-96-9; [Cp*Re(CO)$_2$(NO)]I, 143294-55-7; Cp*Re(CO)$_2$(NO)I, 133670-97-0; [CpRe(CO)$_2$(NO)][BF$_4$], 31960-40-4; [Cp*Re(CO)$_2$(NO)][BF$_4$], 86497-29-2.