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Reactions of Nitridorhenium(V) and -Osmium(VI) Complexes with Acylating Agents

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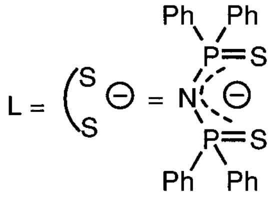
Interaction of Re(N)L$_2$ [L = N(PSPh$_2$)$_2$] **1** with (CF$_3$CO)$_2$O or RCOCl afforded air-sensitive acylimido-Re(V) complexes *trans*-Re[NC(O)CF$_3$](OCOCF$_3$)L$_2$ **2** or *trans*-Re[NC(O)R]ClL$_2$ (R = CCl$_2$H **3**, CClH$_2$ **4**, CH$_3$ **5**), respectively. Treatment of **1** with (CX$_3$CO)$_2$O followed by recrystallization from CH$_2$Cl$_2$/hexane in air led to the formation of the corresponding parent imido complexes *trans*-Re(NH)(OCOCX$_3$)L$_2$ (X = F **6**, Cl **7**). The structure of **7** has been characterized by X-ray crystallography. The Re−N, average Re−S, and Re−O distances are 1.664(3), 2.441, and 2.116(3) Å, respectively. Deprotonation of **6** or **7** with Et$_3$N gave **1**. Recrystallization of **3** from CH$_2$Cl$_2$/hexane in air resulted in oxo-imido exchange and the isolation of the oxo-Re(V) species *trans*-Re(O)ClL$_2$. Treatment of **1** with tosyl anhydride gave *trans*-Re(NH)(OTs)L$_2$ (OTs = tosyl) **8**. Reaction of [*n*-Bu$_4$N][OsNCl$_4$] with KL afforded *trans*-Os(N)ClL$_2$ **9**, which has been characterized by X-ray crystallography. The Os−N, Os−Cl, and average Os−S bond distances in **9** are 1.64(1), 2.577(4), and 2.429 Å, respectively. Treatment of **10** with (CF$_3$CO)$_2$O, Ag(CF$_3$CO$_2$), or CF$_3$CO$_2$H resulted in chloride substitution and the formation of *trans*-Os(N)(OCOCF$_3$)L$_2$ **10**. The Os−N, Os−O, and average Os−S distances in **10** are 1.643(5), 2.271(4), and 2.419 Å, respectively. Treatment of **1** with [Ph$_3$C]BF$_4$ resulted in the isolation of *trans*-Re(NCPh$_3$)(F)L$_2$ **11**, presumably via the cationic tritylimido intermediate [Re(NCPh$_3$)L$_2$]$^+$. Reaction of **9** with [Ph$_3$C]BF$_4$ led to chloride abstraction and the formation of five-coordinate [Os(N)L$_2$]BF$_4$ **12**. The Os−N and average Os−S distances in **12** are 1.646(5) and 2.364 Å, respectively.

Introduction

Acylimido−metal complexes [M = NC(O)R] have attracted much attention due to their applications in metal-mediated nitrogen atom transfer reactions. Groves and co-workers first reported that trifluoroacetylimido-Mn(V) species, which were prepared in situ from nitrido-Mn(V) porphyrins and trifluoroacetic anhydride, react with olefins to give trifluoroacylaziridines and Mn(III) porphyrins.[1] More recently, this reaction was applied to organic synthesis by Carreira and co-workers, who used nitrido-Mn(salen) complexes in conjunction with trifluoroacetic anhydride as reagents for amination of electron-rich olefins including silyl enol ethers and glycals.[2] Acetylimido-Os(VIII) species have also been implicated as the active species for the Os-mediated aminohydroxylation of olefins.[3] Nevertheless in contrast to organoimido−metal (M=NR, R = alkyl or aryl) complexes, there are very few acylimido−metal complexes reported in the literature. Isolated acylimido complexes include Mo[NC(O)Ph](Et$_2$dtc)$_3$ (Et$_2$dtc = *N,N′*-diethyldithiocarbamate),[4] Tp′W^{IV}(CO)Cl[NC(O)CH$_3$],[5] Tp′W^{IV}(CO)(SPh)[NC(O)CH$_3$] (Tp′ = hydridotris(3,5-dimethylpyrazol-1-yl)borate),[6] and W^{VI}Cl$_2$[NC$_6$H$_3$(*i*-Pr)$_2$-2,6][NC(O)C$_6$H$_4$Me-4](OPMe$_3$)(PMe$_3$).[7] To understand the factors governing metal-mediated acylimido transfer, we set out to synthesize acylimido-Re(V) complexes, which are expected to be more stable than the Mn(V) congeners. Although nitrido-Re(V) complexes are known to be nucleophilic and react with electrophiles to give *μ*-nitrido or imido complexes,[8−10] as far as we are aware, there are no reports on the reaction of nitrido-Re(V) with acetylating agents. We are particularly interested in nitrido-Re(V) complex containing bis(diphenylthiophosphoryl)amide (L, Scheme 1),[10] which has been reported to form adduct with BCl$_3$. Herein we describe the

Scheme 1



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reactions of Re(N)L_2 and isoelectronic *trans*-Os(N)ClL_2 with acylating agents and the characterization of the resulting imido or nitrido species.

Experimental Section

General Considerations. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300, 282.4, and 121.5 MHz for ^{1}H, ^{19}F, and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $Si(CH_3)_4$ (^{1}H), $CF_3C_6H_5$ (δ − 64) (^{19}F), and H_3PO_4 (^{31}P). Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer and mass spectra on a Finnigan TSQ 7000 spectrometer. Elemental analyses were performed by Medac Ltd., Surrey, UK.

Solvents were purified by standard procedures and distilled prior to use. All manipulations, unless otherwise stated, were carried out under nitrogen using standard Schlenk techniques. Re(N)L_2 **1**[10] and [n-Bu_4N][$OsNCl_4$][11] were prepared according to the literature methods. KL was synthesized by deprotonation of HL[12] with potassium *tert*-butoxide in methanol. $(CF_3CO)_2O$, $(CCl_3CO)_2O$, $(CHCl_2CO)Cl$, $CH_2ClCOCl$, CH_3COCl, and tosyl anhydride were purchased from Aldrich and used as received.

Preparation of *trans*-Re(NCOCF$_3$)(OCOCF$_3$)L$_2$ 2. To a solution of **1** (80 mg, 0.07 mmol) in CH_2Cl_2 (15 mL) at −10 °C was added $(CF_3CO)_2O$ (0.1 mmol, 0.1 mL of a 1 M solution in CH_2Cl_2) under nitrogen. The reaction mixture was warmed to room temperature and stirred for 30 min. Concentration (to ca. 5 mL) and addition of hexane resulted in the formation of an orange solid (yield 70 mg, 79%). ^{1}H NMR ($CDCl_3$): δ 7.30−7.77 (m, phenyl protons). ^{19}F NMR ($CDCl_3$): δ −72.3 (s, NCOC*F*$_3$), −76.8 (OCOC*F*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 51.2 (s). IR (cm^{-1}, Nujol): 1698, 1710 [ν(C═O)], 1050 sh ([ν(Re═N)]. Anal. Calcd for $C_{52}H_{40}N_3F_6O_3P_4S_4Re$: C, 47.8; H, 3.1; N, 3.2. Found: C, 47.7; H, 3.2; N, 3.4.

Preparation of *trans*-Re(NCOCHCl$_2$)(Cl)L$_2$ 3. To a solution of **1** (100 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added 1 equiv of $CHCl_2COCl$, and the mixture was slowly warmed to room temperature and stirred for 30 min. Addition of hexane (40 mL) afforded an orange solid, which was collected and washed with hexane (yield 90 mg, 80%). ^{1}H NMR ($CDCl_3$): δ 7.30−7.77 (m, phenyl protons). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 51.23 (s). IR (cm^{-1}, Nujol): 1716 [ν(C═O)]. MS (FAB): *m/z* 1208 (M$^+$ − Cl). Anal. Calcd for $C_{50}H_{41}Cl_3N_3OP_4S_4Re{\cdot}CH_2Cl_2$: C, 46.1; H, 3.2; N, 3.2. Found: C, 46.3; H, 3.2, H, 3.1.

Reaction of 1 with CClH$_2$COCl. To a solution of **1** (20 mg) in $CDCl_3$ (0.5 mL) at 0 °C was added $CClH_2COCl$ (0.05 mL), and the resulting red mixture was warmed to room temperature and analyzed by NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ 3.04 (s, 2H, CCl*H*$_2$CO), 7.19−7.85 (m, 40H, phenyl protons). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 48.52 (s).

Reaction of 1 with CH$_3$COCl. This was done as for $CClH_2COCl$ using CH_3COCl (0.05 mL) in place of $CH_2ClCOCl$. The resulting red solution mixture was analyzed by NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ 2.08 (C*H*$_3$CO), 7.19−7.85 (m, 40H, phenyl). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 56.25 (s).

Preparation of *trans*-Re(NH)(OCOCF$_3$)L$_2$ 6. A solution of **2** (100 mg, 0.08 mmol) in CH_2Cl_2/Et_2O was left to stand in air overnight. The green crystals formed were collected and washed with Et_2O (yield 100 mg, 88%). Alternatively, **6** was obtained in good yield by treatment of **1** in CH_2Cl_2 with $(CF_3CO)_2O$, followed by recrystallization from CH_2Cl_2/hexane in air for 1 d. ^{1}H NMR ($CDCl_3$): δ 7.34−7.85 (m, phenyl protons). ^{19}F NMR ($CDCl_3$): δ −76.8 (s, CO$_2$C*F*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 44.8 (s). IR (cm^{-1}, Nujol): 3045 w br [ν(N−H)], 1708 [ν(C═O)], 1073 sh [ν(Re═N)]. Anal. Calcd for $C_{50}H_{41}N_3F_3O_2P_4S_4Re{\cdot}CH_2Cl_2$: C, 47.2; H, 3.3; N, 3.2. Found: C, 47.9; H, 3.3; N, 3.5.

Preparation of *trans*-Re(NH)(OCOCCl$_3$)L$_2$ 7. To a solution of **1** (80 mg, 0.07 mmol) was added $(CCl_3CO)_2O$ (0.1 mol), and the mixture was stirred at room temperature for 1 h. The solvent was pumped off and the residue washed with hexane. Recrystallization from CH_2Cl_2/Et_2O in air afforded green crystals, which were collected and washed with Et_2O (yield: 0.1 g, 88%). ^{1}H NMR ($CDCl_3$): δ 7.30−7.82 (m, phenyl protons). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 44.68 (s). IR (cm^{-1}, KBr): 3045 w [ν(N−H)], 1700 [ν(C═O)]. Anal. Calcd for $ReC_{50}H_{41}N_3Cl_3O_2P_4S_4$: C, 44.4; H, 2.9; N, 3.0. Found: C, 44.7; H, 3.5; N, 2.0.

Preparation of *trans*-Re(NH)(OTs)L$_2$ (Ts = tosyl) 8. To a solution of **1** (80 mg, 0.07 mmol) in CH_2Cl_2 (20 mL) was added tosyl anhydride (24 mg, 0.07 mmol), and the reaction mixture was stirred under nitrogen at room temperature overnight. The solvent was pumped off and the residue was washed with Et_2O. Recrystallization from CH_2Cl_2/hexane in air afforded yellowish green crystals (yield 14 mg, 15%) along with unreacted **1**. ^{1}H NMR (CD_2Cl_2): δ 2.27 (s, 3H, *p*-Me), 6.82 (d, 2H, H$_m$), 7.91 (d, 2H, H$_o$), 7.23−7.79 (m, 40H, phenyl protons). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 45.04 (s).

Preparation of *trans*-Os(N)ClL$_2$ 9. To a solution of [n-Bu_4N][$OsNCl_4$] (0.05 g, 0.09 mmol) in methanol (20 mL) was added KL (0.11 g, 0.23 mmol), and the mixture was stirred at room temperature for 2 h. The orange solid was collected, washed with methanol, and recrystallized from CH_2Cl_2/Et_2O (yield 60%). ^{1}H NMR ($CDCl_3$): δ 7.23−7.83 (m, phenyl protons). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 40.4 (s). IR (Nujol, cm^{-1}): 1064 [ν(Os≡N)]. Anal. Calcd for $C_{48}H_{40}NClP_4S_4$-Os: C, 50.7; H, 3.5; N, 3.7. Found: C, 50.6; H; 3.6; N, 3.7.

Preparation of *trans*-Os(N)(OCOCF$_3$)L$_2$ 10. To a solution of **9** (100 mg, 0.09 mmol) in CH_2Cl_2 (20 mL) was added $(CF_3CO)_2O$ (0.1 mmol, 1 mL of 1 M solution in CH_2Cl_2), and the mixture was stirred at room temperature for 1 h. The solvent was pumped off and the residue washed with hexane. Recrystallization of the residue from CH_2Cl_2/Et_2O afforded air-stable orange crystals (yield 78 mg, 70%). Alternatively **10** could be prepared in similar yield by treatment of **9** with 1 equiv of $Ag(CF_3CO_2)$ or CH_3CO_2H. ^{1}H NMR (CD_2Cl_2): δ 7.24−7.83 (m, phenyl protons); ^{19}F NMR (CD_2Cl_2): δ −76.3 (s). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.18 (s). IR (cm^{-1}, Nujol): 1696 [ν(C═O)], 1082 [ν(Os≡N)]. Anal. Calcd for $C_{50}H_{41}N_3ClF_3O_2P_4S_4Os$: C, 48.0; H, 3.3; N, 3.4. Found: C, 48.4; H, 3.4; N, 3.3.

Preparation of *trans*-Re(NCPh$_3$)(F)L$_2$ 11. To a solution of **1** (80 mg, 0.07 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added 1 equiv of [Ph_3C](BF_4) (24 mg, 0.07 mmol), and the reaction mixture was stirred at room temperature overnight. The solvent was pumped off and the residue was extracted with Et_2O. Recrystallization from Et_2O/hexane afforded pale purple crystals (yield 50 mg, 53%). ^{1}H NMR ($CDCl_3$): δ 6.69−7.90 (m, phenyl protons). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 40.61 (s). ^{19}F NMR ($CDCl_3$): δ −86 (s). IR (cm^{-1}, Nujol): 1192 sh [ν(Re═N)]. FAB MS: 1359 (M + 1)$^+$. Anal. Calcd for $ReC_{67}H_{55}FN_3P_4S_4$: C, 59.2; H, 4.1; N, 3.1. Found: C, 58.4; H, 4.3; N, 2.9.

Preparation of [Os(N)L$_2$](BF$_4$) 12. To a solution of **9** (100 mg, 0.09 mmol) in CH_2Cl_2 (20 mL) was added 1 drop of HBF_4 (1M in Et_2O). After stirring at room temperature for 1 h, the solvent was pumped off and the residue washed with Et_2O. Recrystallization from CH_2Cl_2/hexane afforded yellow crystals, which are suitable for X-ray diffraction study (yield 73 mg, 70%). Alternatively **11** could be isolated in similar yield by treatment of **9** with [Ph_3C](BF_4). ^{1}H NMR ($CDCl_3$): δ 7.34−7.84 (m, phenyl protons); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 36.41 (s). MS (FAB): *m/z* 1102 (M$^+$ − BF_4). Anal. Calcd. for $C_{48}H_{40}BF_4N_3OsP_4S_4$: C, 45.0; H, 3.3; N, 3.2. Found: C, 44.5; H, 3.1; N, 3.0%.

X-ray Crystallography. A summary of pertinent crystallographic data and experimental details for complexes **7**·CH_2Cl_2, **9**·CH_2Cl_2, **10**·$2CH_2Cl_2{\cdot}C_6H_{14}$, and **12**·$1.5CH_2Cl_2$ are listed in Table 1. Data were collected on a MAR-Research image-plate diffractometer (for **7**·CH_2Cl_2), Rigaku AFC7R diffractometer (for **9**·CH_2Cl_2), and Siemens P4 dffractometer (for **10**·$2CH_2Cl_2{\cdot}C_6H_{14}$ and **12**·$1.5CH_2Cl_2$) using graphite-monochromated radiation (λ = 7.0073 Å). All intensities were corrected for Lorentz and polarization effects. An approximation to absorption correction was also applied. The structures were solved by direct methods and refined by full matrix least-squares analysis. Non-hydrogen atoms for **7**•CH_2Cl_2 and **10**·$2CH_2Cl_2{\cdot}C_6H_{14}$ were refined anisotropically while those for **12**·$1.5CH_2Cl_2$ were refined isotropically. For **9**, the Os, Cl, P, and S atoms were refined anisotropically while the remaining non-hydrogen atoms were refined isotropically. For **7**•CH_2Cl_2, the hydrogen atom on imido group was located by difference Fourier synthesis based on low angle data (θ < 15°) while hydrogen

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Table 1. Crystal Data and Experimental Details for *trans*-Re(NH)$L_2(CCl_3CO_2)\cdot CH_2Cl_2$ (**7**$\cdot CH_2Cl_2$), *trans*-Os(N)Cl$L_2\cdot CH_2Cl_2$ (**9**$\cdot CH_2Cl_2$), *trans*-Os(N)$(OCOCF_3)L_2\cdot C_6H_{14}\cdot 2CH_2Cl_2$ (**10**$\cdot C_6H_{14}\cdot 2CH_2Cl_2$), and *trans*-$[Os(N)L_2]BF_4\cdot 1.5CH_2Cl_2$ (**12**$\cdot 1.5CH_2Cl_2$)

	7$\cdot CH_2Cl_2$	**9**$\cdot CH_2Cl_2$	**10**$\cdot C_6H_{14}\cdot 2CH_2Cl_2$	**12**$\cdot 1.5CH_2Cl_2$
empirical formula	$C_{51}H_{43}N_3Cl_5O_2P_4S_4Re$	$C_{49}H_{42}NCl_3P_4S_4Os$	$C_{58}H_{58}Cl_4F_3N_3O_2P_4S_4Os$	$C_{49.5}H_{40}BCl_3F_4N_3P_4S_4Os$
formula weight	1345.53	1221.59	1470.2	1312.3
crystal system	monoclinic	triclinic	triclinic	monoclinic
a, Å	14.009(1)	11.475(1)	12.967(4)	13.464(2)
b, Å	16.850(1)	17.493(2)	15.943(5)	24.618(2)
c, Å	25.528(2)	25.697(4)	16.468(5)	17.083(2)
α, deg		86.12(2)	80.70(2)	
β, deg	99.43(2)	84.83(2)	72.67(3)	95.72(2)
g, deg		86.85(2)	70./27(2)	
V, $Å^3$	5478.8(7)	5119(1)	3052.2(16)	5714.9(12)
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	Cc
Z	4	4	2	4
ρ_{calcd}, g cm^{-3}	1.631	1.585	1.600	1.525
temperature, °C	25	25	−70	25
$F(000)$	2680	2432	1476	2600
μ(Mo Kα), cm^{-1}	27.75	29.71	25.6	26.78
no. of observation	7758 ($I > 3.0\sigma(I)$)	8074 ($I > 3.0\sigma(I)$)	7832 ($F > 4.0\sigma(F)$)	7375 ($F > 4.0\sigma(F)$)
no. of variables	631	633	680	629
weighing factor	$1/[\sigma^2(F_o) + 0.023F_o^2/4]$	$1/\sigma^2(F_o)$	$1/[\sigma^2(F_o) + 0.0003F_o^2]$	$1/[\sigma^2(F_o) + 0.0003F_o^2]$
R, %	3.2	4.6	4.44	3.87
R_w, %	3.7	4.6	4.74	4.28
goodness of fit	1.58	2.11	1.30	1.32

[a] $R = (\sum|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] Goodness of fit $= [(\sum w|F_o| - |F_c|)^2/\sum N_{obs} - N_{param}]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans*-Re(NH)$(OCOCCl_3)L_2\cdot CH_2Cl_2$ (**7**$\cdot CH_2Cl_2$)

Bond Lengths			
Re(1)−S(1)	2.472(1)	Re−S(2)	2.398(1)
Re(1)−S(3)	2.480(1)	Re(1)−S(4)	2.412(1)
Re(1)−O(1)	2.116(3)	Re(1)−N(1)	1.664(3)
S(1)−P(1)	2.043(2)	S(2)−P(2)	2.058(2)
S(3)−P(3)	2.071(2)	S(4)−P(4)	2.053(2)
P(1)−N(1)	1.600(3)	P(2)−N(1)	1.591(4)
P(3)−N(2)	1.588(4)	P(4)−N(2)	1.577(3)
Bond Angles			
S(1)−Re(1)-S(2)	97.67(3)	S(1)−Re(1)-S(3)	84.17(4)
S(1)−Re(1)-S(4)	171.60(4)	S(1)−Re(1)-O(1)	85.71(8)
S(1)−Re(1)-N(3)	92.1(1)	S(2)−Re(1)-S(3)	161.49(4)
S(2)−Re(1)-S(4)	77.16(4)	S(2)−Re(1)-O(1)	84.15(7)
S(2)−Re(1)-N(3)	102.63(9)	S(3)−Re(1)-S(4)	98.64(4)
S(3)−Re(1)-O(1	77.60(7)	S(3)−Re(1)-N(3)	95.69(9)
S(4)−Re(1)-O(1)	87.17(8)	S(4)−Re(1)-N(3)	95.5(1)
O(1)−Re(1)-N(3)	173.1(1)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans*-Os(N)Cl$L_2\cdot CH_2Cl_2$ (**9**$\cdot CH_2Cl_2$)

Bond Lengths			
Os(1)−Cl(2)	2.577(4)	Os(1)−S(1)	2.417(4)
Os(1)−S(2)	2.454(4)	Os(1)−S(3)	2.444(4)
Os(1)−S(4)	2.399(3)	Os(1)−N(3)	1.64(1)
Bond Angles			
Cl(2)−Os(1)-S(1)	87.3(1)	Cl(2)−Os(1)-S(2)	80.3(1)
Cl(2)−Os(1)-S(3)	79.3(1)	Cl(2)−Os(1)-S(4)	87.3(1)
Cl(2)−Os(1)-N(3)	172.6(4)	S(1)−Os(1)-S(2)	98.1(1)
S(1)−Os(1)-S(3)	165.6(1)	S(1)−Os(1)-S(4)	77.5(1)
S(1)−Os(1)-N(3)	97.4(4)	S(2)−Os(1)-S(3)	84.9(1)
S(2)−Os(1)-S(4)	167.0(1)	S(2)−Os(1)-N(3)	93.4(4)
S(3)−Os(1)-S(4)	96.5(1)	S(3)−Os(1)-N(3)	96.5(4)
S(4)−Os(1)-N(3)	97.4(4)	Os(1)−S(1)-P(1)	109.9(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for *trans*-Os(N)$(OCOCF_3)L_2\cdot CH_2Cl_2\cdot C_6H_{14}$ (**10**$\cdot CH_2Cl_2\cdot C_6H_{14}$)

Bond Lengths			
Os−S(1)	2.410(2)	Os−S(2)	2.443(2)
Os−S(3)	2.430(2)	Os−S(4)	2.403(2)
Os−O(1)	2.271(4)	Os−N(2)	1.643(5)
Bond Angles			
S(1)−Os-S(2)	96.0(1)	S(1)−Os-S(3)	163.9(1)
S(1)−Os-S(4)	77.3(1)	S(1)−Os-O(1)	80.9(1)
S(1)−Os-N(2)	177.1(3)	S(2)−Os-S(3)	85.0(1)
S(2)−Os-S(4)	163.5(1)	S(2)−Os-O(1)	81.2(2)
S(2)−Os-N(2)	95.9(3)	S(3)−Os-S(4)	97.3(1)
S(3)−Os-O(1)	83.4(1)	S(3)−Os-N(2)	97.0(2)
S(4)−Os-O(1)	82.8(2)	S(4)−Os-N(2)	100.0(2)
O(1)−Os-N(2)	177.1(3)		

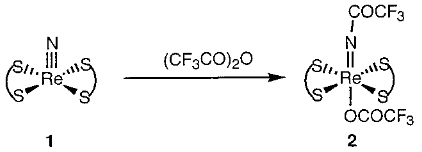
Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[Os(N)L_2](BF_4)\cdot 1.5CH_2Cl_2$ (**12**$\cdot 1.5CH_2Cl_2$)

Bond Lengths			
Os−S(4)	2.357(5)	Os−S(2)	2.373(4)
Os−S(3)	2.401(4)	Os−S(1)	2.325(4)
Os−N(3)	1.646(5)		
Bond Angles			
S(4)−Os-S(3)	94.9(1)	S(4)−Os-S(2)	75.5(2)
S(4)−Os-S(1)	141.2(2)	S(4)−Os-N(3)	110.0(6)
S(3)−Os-S(2)	154.9(2)	S(3)−Os-S(1)	76.8(1)
S(3)−Os-N(3)	102.6(6)	S(2)−Os-S(1)	96.0(1)
S(2)−Os-N(3)	102.5(6)	S(1)−Os-N(3)	108.8(6)

atoms on the organic moieties were generated in their idealized positions (C−H, 0.95 Å). In the crystal structure of **12**$\cdot 1.5CH_2Cl_2$, the BF_4 counteranion is disordered. Two CH_2Cl_2 molecules were found in partial occupancy and were refined as 75%. Selected bond lengths and angles for **7**, **9**, **10** and **12** are listed in Tables 2, 3, 4, and 5, respectively.

Results

Acylimido Complexes of Re(V). Treatment of yellow **1** in CH_2Cl_2 with a slight excess of $(CF_3CO)_2O$ gave an orange solution, from which the trifluoroacetylimido-Re(V) species *trans*-Re$[NC(O)CX_3](OCOCX_3)L_2$ **2** was isolated as an analytically pure solid (eq 1).

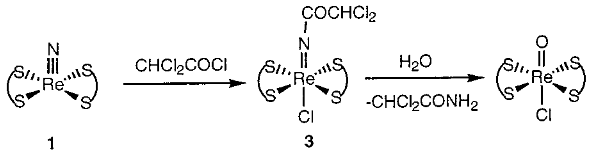


1 **2**

(1)

The course of reaction has been monitored by ^{31}P and ^{19}F NMR spectroscopy. Upon addition of 1 equiv of $(CF_3CO)_2O$ to **1** in $CDCl_3$, the signals for $(CF_3CO)_2O$ (δ^F −75.5) and **1** (δ^P 38.0) disappeared and a new species **2** (δ^F −72.3−76.8; δ^P 51.2) was formed. Complex **2** is stable in the solid state but decomposes readily in solution to give a green species, identified as a Re(V) parent imido species (see below). However, in the presence of excess $(CF_3CO)_2O$, **2** is stable in solution for hours. The IR spectrum of **2** shows two C═O bands at 1698 and 1710 cm^{-1}, assignable to acyl and acetate groups. Unlike acylimido-Mn(V) complexes, no reactions of **2** with olefins (e.g., styrene) or silyl enol ethers (e.g., 2-methyl-1-(trimethylsilyloxyl)-1-propene) were observed.

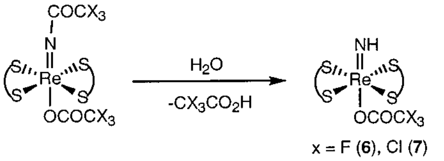
Alternatively, acylimido-Re(V) complexes can be prepared by reaction of nitrido-Re(V) with acyl chlorides. Thus, treatment of **1** with CCl_2HCOCl in CH_2Cl_2 afforded *trans*-Re[NC(O)-CCl_2H]ClL_2 **3**, isolated as an orange solid. Complex **3** is air stable in the solid state but is somewhat moisture sensitive in solutions. However, unlike **2**, hydrolysis of **3** yielded the known oxo-Re(V) species *trans*-Re(O)ClL_2,[13] which was identified by IR spectroscopy and elemental analysis, instead of the parent imido species. The oxo-Re(V) species is apparently formed via oxo-imido exchange of **3** because the organic product CCl_2-HC(O)NH_2 has been identified by NMR and IR spectroscopy (eq 2).



(2)

The ν(C═O) for **3** of 1716 cm^{-1} is higher than those for **2**. Similarly, treatment of **1** with RCOCl gave the respective acylimido species Re[NC(O)R]ClL_2 (R = CH_2Cl **4**, CH_3 **5**), which hydrolyze readily to give *trans*-Re(O)ClL_2.

Parent Imido Complex of Re(V). Attempts to recrystallize **2** from CH_2Cl_2/Et_2O led to isolation of the green parent imido-Re(V) complex *trans*-Re(NH)($OCOCF_3$)L_2 **6**, which could also be synthesized directly by the reaction of **1** with $(CF_3CO)_2O$ followed by recrystallization in air. Similarly, treatment of **1** with $(CCl_3CO)_2O$ followed by recrystallization from CH_2Cl_2/hexane in air afforded the trichloroacetate compound *trans*-Re(NH)($OCOCCl_3$)L_2 **7**. Apparently, these parent imido-Re(V) complexes were formed by hydrolysis of the acylimido-Re(V) species by the trace amount of water in solvent because addition of water to **2** in $CDCl_3$ at −40 °C gave **6** immediately (eq 3).



(3)

The IR spectrum of **6** shows the CO band at 1708 cm^{-1}, assignable to the acetate ligand. The IR CO bands for **2** at 1698 and 1710 cm^{-1} are therefore assigned to the acyl and acetate groups, respectively.

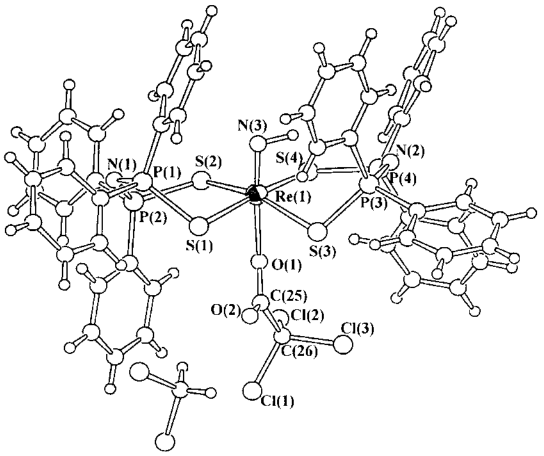


Figure 1. Perspective view of *trans*-Re(NH)(CCl_3CO_2)L_2 (**7**).

The solid-state structure of **7** has been established by X-ray crystallography. Figure 1 shows a perspective view of **7**; selected bond lengths and angles are listed in Table 2. To our knowledge, **7** is the second structurally characterized parent imido-Re complex; the first example being $ReCl_2(NH)(NHNH_2)(PPh_3)_2$.[14] The Re−N distance in **7** of 1.664(3) Å is only slightly longer than that for **1** (1.647(7) Å)[10] but is shorter than that for $ReCl_2(NH)(NHNH_2)(PPh_3)_2$ (1.712(8) Å).[14] Nevertheless, the Re−N distance in $ReCl_2(NH)(NHNH_2)(PPh_3)_2$ is long apparently due to strong trans influence of the hydrazido ligand. It might be noted that the Re−N distance in **7** is closer to that in the BCl_3 adduct Re($NBCl_3$)L_2 (1.672(3) Å)[10] than to those typical for organoimido-Re(V) complexes, e.g., $Re(NPh)Cl_3(PPh_3)_2$ (1.726(6) Å),[15] which contain nitrogen−carbon covalent bonds. This Re−N bond distance may suggest the resonance structure $Re{\equiv}N^{\delta-}{-}H^{\delta+}$ for **7**. In other words, the imido nitrogen in **7** has a strong nitride character. The imido hydrogen was located by difference Fourier synthesis, and the N−H distance and Re−N−H angle for **7** are estimated to be 1.0 Å and 103.1°, respectively. The formulation of **7** as a nitrido-Re(V) complex of protonated L is ruled out because the P═S and P−N distances in **7** are very similar to those found in Re($NBCl_3$)L_2, which contains deprotonated L.[10] Moreover a single ^{31}P resonant signal was observed for **7** at temperatures down to −50 °C, suggesting that all the P═S bonds should be equivalent. Despite numerous attempts, we were not able to observe the imido hydrogen of **7** by ^1H NMR spectroscopy probably due to protic character of imido hydrogen. Previously it was reported that the NH proton signal for Mo(NH)(OTf)(*syn*-Me_8[16]aneS_4)}OTf (Me_8[16]-aneS_4 = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane, OTf = triflate) occurs at δ 7.49.[16] Therefore it is possible that the NH signal for **7** may also lie in this region, which happens to overlap with the phenyl proton signals of L. The IR (KBr) spectrum of **7** shows a weak peak at 3045 cm^{-1}, which may be tentatively assigned as ν(N−H). This stretching frequency is lower than those found for Mo(NH)(OTf)(*syn*-Me_8[16]aneS_4)}OTf (3100 cm^{-1})[16] and $ReCl_2(NH)(NHNH_2)$-$(PPh_3)_2$ (3125 and 3330 cm^{-1})[14] probably due to protic character of imido hydrogen. As expected, **6** and **7** are acidic and can be depronotated by bases such as Et_3N to give **1.** It may be noted that acid−base chemistry of parent imido complexes of Mo[17] and Re[18] is well documented.

In an attempt to synthesize tosylimido-Re(V) complexes, reaction of tosyl anhydride with **1** was studied. Treatment of **1**

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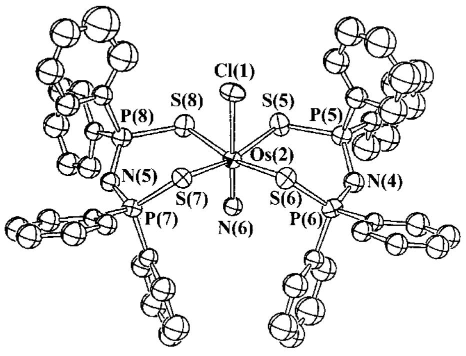
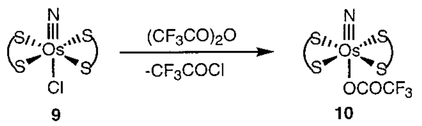


Figure 2. Perspective view of *trans*-Os(N)ClL$_2$ (**9**).

with tosyl anhydride for 2 days gave a yellow solution, from which *trans*-Re(NH)L$_2$(OTs) **8** was obtained in low yield, along with the unreacted **1**. The parent imido complex **8** was apparently formed from hydrolysis of the unisolated tosylimido intermediate *trans*-Re(NTs)(OTs)L$_2$. The reaction of **1** with tosyl anhydride is slower than that with $(CF_3CO)_2O$ possibly because tosyl is a worse leaving group than CF_3CO_2.

Acylation of Nitrido-Os(VI). To compare the nucleophilicity of nitrido-Re(V) with the isoelectronic nitrido-Os(VI) analogue, the nitrido-Os (VI) complex of L was synthesized. Treatment of [*n*-Bu$_4$N][OsNCl$_4$] with 2 equiv of KL afforded *trans*-[Os(N)ClL$_2$] **9**, isolated as air-stable orange crystals. The structure of **9** has been confirmed by X-ray crystallography. Figure 2 shows a diagram of the molecule; selected bond lengths and angles are given in Table 3. The Os−N and average Os−S distances in **9** are 1.64(1) and 2.428 Å, respectively. The Os−N distance for **9** is similar to that in $[OsN(mnt)_2]^-$ (Os−N = 1.639(8) Å, mnt = maleonitriledithiolate).[19] The Os−Cl distance in **9** of 2.577(4) Å is longer than that in *trans*-[Os(tpy)(N)Cl$_2$]$^+$ [Os−Cl (trans to Cl) = 2.346 Å, tpy = 2,2′:6′,2″-terpyridine][20] due to strong trans influence of the nitride. The chloride in **9** is therefore expected to be substitutionally labile (see below). The Os is situated at ca. 0.286 Å above mean S$_4$ plane, which is less than that for 5-coordinate **1** (0.55 Å).[10]

Treatment of **9** with $(CF_3CO)_2O$ resulted in color change from orange to yellow, from which a yellow solid **10** was isolated. The ^{19}F and ^{31}P NMR spectroscopy shows that **9** (δ^P 40.4) reacts cleanly with $(CF_3CO)_2O$ (δ^F −75.5) to give **10** (δ^P 36.5, δ^F −76.3). Furthermore, the IR spectrum of **10** shows ν(C=O) at 1696 cm^{-1}, indicative of the presence of trifluoroacetate. Complex **10** was unambiguously identified as a nitrido(trifluoroacetato)-Os(VI) complex, *trans*-Os(N)(OCOCF$_3$)L$_2$, by X-ray diffraction study. $(CF_3CO)_2O$ abstracts chloride instead of attacking the nitride of **9** (eq 4) apparently because the Os≡N is not sufficiently basic and the chloride is labile.



(4)

The organic product CF$_3$COCl of the reaction was not characterized. Consistent with the lability of chloride, **10** was obtained in good yield from the reaction of **9** with Ag(CF$_3$CO$_2$) or CF$_3$CO$_2$H. The molecular structure of **10** is shown in Figure 3; selected bond lengths and angles are listed in Table 4. The Os−N and average Os−S distances (1.643(5) and 2.421 Å, respectively) are similar to those for **9**. The Os−O distance of 2.271(4) Å is longer than those in K[OsO$_2$(O$_2$CCH$_3$)$_3$] (average 2.026 and 2.148 Å for mono- and bidentate acetates, respectively)[21] due to trans influence of nitride.

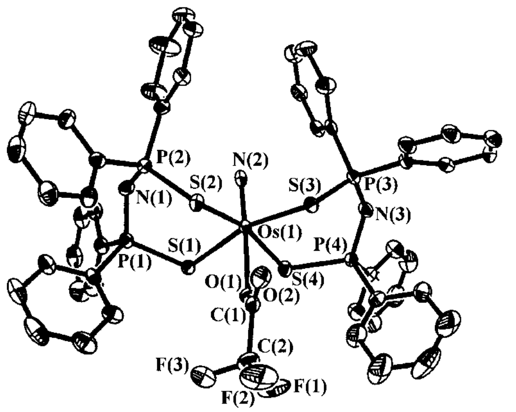
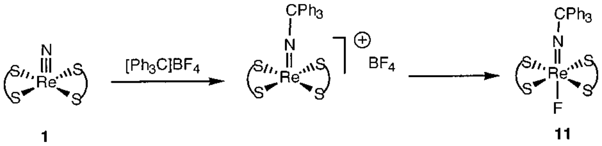


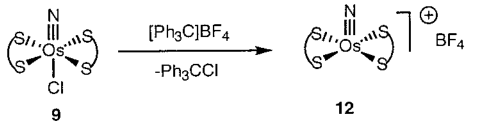
Figure 3. Perspective view of *trans*-Os(N)(OCOCF$_3$)L$_2$ (**10**).

Alkylation of Nitrido-Re(V) and -Os(VI). Treatment of **1** with [Ph$_3$C](BF$_4$) led to isolation of the tritylimido complex *trans*-Re(NCPh$_3$)(F)L$_2$ **11**. The presence of fluoride in **11** is confirmed by mass spectrometry and ^{19}F NMR spectroscopy (δ^F −86). It seems likely that alkylation of **1** initially gave the cationic 16e tritylimido intermediate *trans*-[Re(NCPh$_3$)L$_2$]$^+$, which abstracts fluoride from BF$_4$ to give **11** (eq 5).



(5)

On the other hand, treatment of **9** with [Ph$_3$C](BF$_4$) afforded the cationic nitrido-Os(VI) complex [Os(N)L$_2$]BF$_4$ **12**, instead of the Os(VI) tritylimido species. Therefore, like $(CF_3CO)_2O$, the trityl ion abstracts chloride instead of alkylating the nitride of **9** (eq 6).



(6)

Alternatively, complex **12** could be synthesized by reaction of **9** with HBF$_4$ or AgBF$_4$, with elimination of HCl and AgCl, respectively. The identity of **12** has been unambiguously established by X-ray crystallography. To our knowledge complex **12** is the first example of cationic 5-coordinate nitrido-Os(VI) complex. It may be noted that cationic nitrido-Os(VI) complexes are usually octahedral. Figure 4 shows a perspective view of **12**; selected bond lengths and angles are listed in Table 5. Complex **12** is isostructural with **1**[10] and has a square pyramidal geometry. The Os−N and average Os−S distances are 1.646 and 2.364 Å, respectively. It appears that the Os−N distance is not very sensitive to the overall charge of the nitrido-Os complexes as the Os−N distances in cationic **12** and neutral **9** and **10** are all very similar. By contrast, the Os−S distances in cationic **12** are significantly shorter than those in **9** and **10**.

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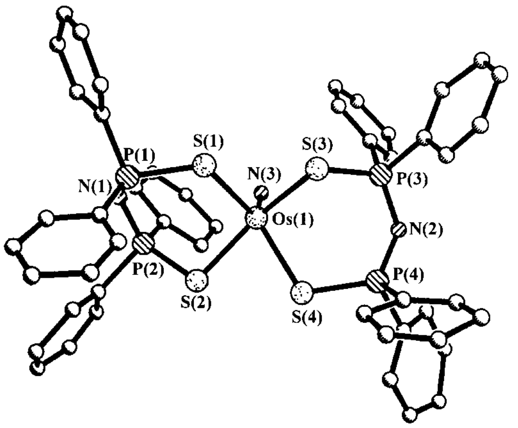

Figure 4. Perspective view of the cation $[Os(N)L_2]^+$.

Discussion

Acylation of Nitrido-Re(V). It is well documented that nitrido-Re(V) complexes are nucleophilic and react with electrophiles to give Re(V) organoimido complexes or adducts of Re(V) nitride. In this work, we found that acylimido-Re(V) species can be obtained by acylation of **1** with $(RCO_2)_2O$ or RCOCl. In contrast to acetylimido-W complexes,[5,6] these acylimido-Re(V) species are moisture sensitive and undergo hydrolysis in solution readily. Interestingly, the product of hydrolysis of Re═NC(O)R was found to be dependent on the substituent R. For highly electron-withdrawing R such as CF_3 and CCl_3, hydrolysis of Re═NC(O)R led to C−N bond cleavage and the formation of Re═NH species. Apparently, the CF_3 and CCl_3 groups render the carbonyl very electrophilic and susceptible to nucleophilic attack by water. A similar finding has been observed for hydrolysis of organic amides: acid hydrolysis of trihaloacetamide is more facile than that for acetamide.[22] By contrast, for less electron-withdrawing R such as $CHCl_2$, CH_2Cl, and CH_3, hydrolysis of Re═NC(O)R yielded Re═O species via oxo-imido exchange. It may be noted that while oxo-imido exchange is well documented for organoimido complexes of earlier transition metals, which are therefore moisture sensitive, C−N bond cleavage for imide ligands is less common and has been observed for organoimido complexes of some later transition metals, e.g., Os,[23,24] Ru,[24] and Mo.[25]

Unlike acylimido-Mn(V) complexes, complex **2** does not undergo imido group transfer with olefins and silyl enol ethers. The difference in reactivity between Mn- and Re-acylimido complexes may be explained in terms of the relative M═N bond strength. The Re═N multiple bond is strong and therefore imido N−C(O)R bond cleavage to give stable Re═NH species is preferred to imido group transfer. Furthermore the Mn(V/III) reduction accompanied by imido group transfer is thermodynamically more feasible than the Re(V/III) counterpart.

Acylation of Nitrido-Os(VI). Attempts to acylate or alkylate the nitrido-Os(VI) complex **9** led to chloride abstraction rather than electrophilic attack on nitride, indicating that nitrido-Os(VI) is less nucleophilic than the isoelectronic nitrido-Re(V) analogue. As a matter of fact, some nitrido-Os(VI) complexes, notably *trans*-$[Os(tpy)(N)Cl_2]^+$, exhibit electrophilic character and react with nucleophiles such as PPh_3,[26] N_3^-, and S_8.[27,28] The low nucleophilicity of nitrido-Os(VI) complexes is attributed to the strong covalent character of Os≡N bond. Alkylation of nitrido-Os(VI) to give imido species has only been observed for $[Os(N)R_4]^-$ (R = alkyl)[29] and $[OsN(bdt)_2]^-$ (bdt = 1,2-benzenedithiolate),[30] which contain strongly electron-releasing alkyl and thiolate ligands, respectively. The microscopic reverse of nitride alkylation, i.e., imido C−N bond cleavage, is, however, well precedented for imido-Os complexes.[23,24]

It is also of interest to compare the stability of cationic 5-coordinate $[Os(N)L_2]^+$ and $[Re(NCPh_3)L_2]^+$. While the former complex is stable for isolation, the latter is believed to be very electrophilic and capable of abstracting fluoride from BF_4^-. This indicates that nitride can stabilize the 16e configuration of Os(VI) by formation of strong Os≡N triple bond. On the other hand, the Re═$NCPh_3$ bond is comparatively weaker and thus the imido-Re(V) complex tends to be octahedral in order to fully utilize the metal d orbitals.

In summary, we have demonstrated that treatment of nitrido-Re(V) with acylating agents affords acylimido-Re(V) species. These acylimido-Re(V) complexes undergo hydrolysis to give parent imido- or oxo-Re(V) species. On the other hand, the nitrido-Os(VI) analogue is not acylated by trifluoroacetic anhydride because of its low nucleophilicity.

Acknowledgment. Support from The Hong Kong University of Science and Technology and The Hong Kong Research Grants Council is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **7**·CH_2Cl_2, **9**·CH_2Cl_2, **10**-C_6H_{14}·CH_2Cl_2, and **12**·1.5CH_2Cl_2, are available via the Internet at http://pubs.acs.org.

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