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A New Route to Coordination Complexes of Nitroxyl (HN═O) via Insertion Reactions of Nitrosonium Triflate with Transition-Metal Hydrides

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Received July 17, 2002

Nitroxyl (HN═O), a simple yet highly reactive molecule, is attracting current research interest primarily because of its relationship to nitric oxide. It has relevance in biochemistry[1] and has been invoked as an intermediate in a variety of photochemical and free-radical reactions,[2] detected in interstellar clouds,[3] and implicated as an intermediate in the combustion of nitrogen-containing fuels and the oxidation of atmospheric nitrogen.[4] Several examples of transition-metal complexes containing the HN═O ligand have been reported, and three distinct preparative routes to nitroxyl derivatives have been described: (i) protonation of nitrosyl ligands in complexes of iridium, iron, osmium, and rhenium,[5−8] (ii) nucleophilic addition of hydride to nitrosyl ligands in ruthenium complexes,[9,10] and (iii) selective oxidation (using $Pb(OAc)_4$) of a rhenium hydroxylamine complex.[11] Diazene (HN═NH) is isoelectronic with nitroxyl, and because 1,1-insertion of aryldiazonium ions into metal−hydride bonds has been known for decades to provide an effective synthesis of aryldiazene complexes,[12] we were intrigued by the possibility that analogous 1,1-insertion reactions of nitrosonium salts with metal-hydrides might afford a facile route to nitroxyl species. This work describes our comparative examination of the reactions of aryldiazonium and nitrosonium salts with several d^6 transition-metal hydrido and methyl complexes, including examples of nitrosonium insertion into M−H and M−R bonds to give coordination complexes containing nitroxyl and nitrosoalkane (RN═O) ligands.

We chose *mer,trans*-$ReH(CO)_3(PPh_3)_2$ (**1**) for our initial studies because the nitroxyl complex [*mer,trans*-$Re(NH{=}O)(CO)_3(PPh_3)_2$][$SO_3CF_3$] is known and exhibits moderate stability.[11] Reaction of acetone solutions of **1** with [PhN_2][PF_6] affords the phenyldiazene complex salt [*mer,trans*-$Re(NH{=}NPh)(CO)_3(PPh_3)_2$][$PF_6$] (**2**) as analytically pure, yellow-orange crystals in 71% yield (eq 1). The parent diazene analogue, [*mer,trans*-$Re(NH{=}NH)(CO)_3(PPh_3)_2$][$SO_3CF_3$], is also known.[13c] Characterization of **2** followed from its IR and ^1H and $^{31}P\{^1H\}$ NMR spectra, elemental analysis, and a single-crystal X-ray diffraction study.[14] The ^1H NMR spectrum of **2** shows a characteristic singlet for the diazenyl proton at δ 12.94 in CD_2Cl_2,[13] and by utilizing an inverse-detection NMR protocol (bilinear rotational decoupling), the $|^1J_{^{15}NH}| = 68.4$ Hz was observed, a typical value for a proton attached to a metal-bound sp^2-hybridized nitrogen.[5−9,11,13,15] A perspective view of the complex cation of **2** is shown in Figure 1; the N(1)−N(2) bond distance (1.245(7) Å) is typical for an N−N double bond and is within the range normally found for aryldiazene complexes (∼1.22 to ∼1.26 Å).[13]

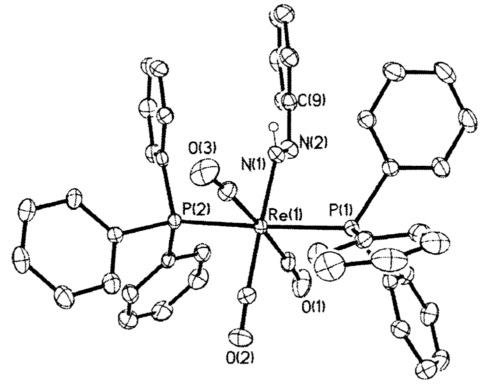
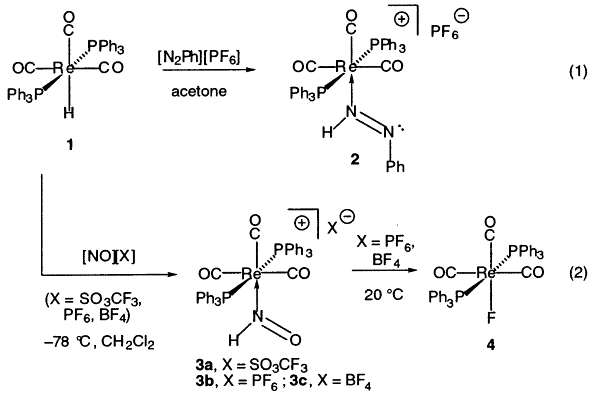


Figure 1. A perspective view of the molecular structure of the complex cation of **2·(0.5Et₂O)**. H-atoms, except that on N(1), have been omitted. Selected metrical parameters: Re(1)−N(1) = 2.149(5), N(1)−N(2) = 1.245(7) Å; Re(1)−N(1)−N(2) = 126.4(4), N(1)−N(2)−C(9) = 118.3(5)°.



Treatment of a cold (−78 °C) methylene chloride solution of **1** with 1 equiv of nitrosonium triflate, [NO][SO_3CF_3], results in clean 1,1-insertion of nitrosonium into the Re−H bond to give [*mer,trans*-$Re(NH{=}O)(CO)_3(PPh_3)_2$][$SO_3CF_3$] (**3a**) as an analytically pure crystalline salt in 86% isolated yield (eq 2).[14] The characterization of **3a** followed by spectroscopic comparison to an authentic sample prepared by the oxidation of [*mer,trans*-$Re(NH_2OH)(CO)_3(PPh_3)_2$][$SO_3CF_3$] by $Pb(OAc)_4$.[11] Of particular note is the diagnostic proton resonance for the HN═O ligand (δ 21.66, CD_2Cl_2). The reaction appears to proceed by direct insertion of NO^+ into the metal−hydride bond, although we cannot exclude a mechanism involving initial intermolecular electron transfer to give [$ReH(CO)_3(PPh_3)_2{}^+$] and $NO^\bullet$ followed by insertion of nitric oxide into the cationic Re−H intermediate; NO has recently been shown to couple with a Ru−H moiety to give a nitroxyl adduct.[10] No other metal products,

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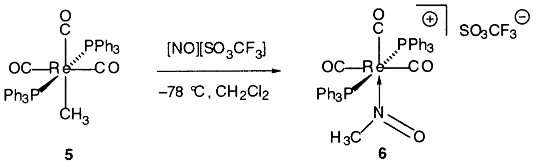
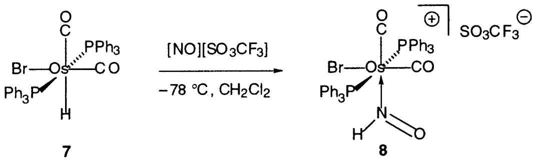
10.1021/ja0277475 CCC: $22.00 © 2002 American Chemical Society

such as those resulting from carbonyl displacement, have been observed. It is noteworthy that NO$^+$ insertion into the Re−H bond of **1** is also observed for the more commonly encountered, commercially available nitrosonium salts [NO][X] (X = PF$_6$, BF$_4$) when the reaction is monitored at low temperature by ^{1}H NMR. However, the resulting hexafluorophosphate and tetrafluoroborate complex salts (**3b** and **3c**) are much less stable than the corresponding trifluoromethanesulfonate derivative **3a**, readily decomposing at ambient temperature to the neutral fluoride complex *mer*,*trans*-ReF(CO)$_3$(PPh$_3$)$_2$ (**4**; eq 2).[16] This observation may explain why related insertion reactions of nitrosonium salts with metal hydrides have not been previously reported.

Reaction of nitrosonium triflate with CH$_2$Cl$_2$ solutions of *mer*,*trans*-Re(CH$_3$)(CO)$_3$(PPh$_3$)$_2$ (**5**) gives the nitrosomethane complex [*mer*,*trans*-Re{N(CH$_3$)═O}(CO)$_3$(PPh$_3$)$_2$][SO$_3$CF$_3$] (**6**) as red crystals in 75% isolated yield (eq 3).[14] Legzdins has reported NO$^+$ insertion into Cr−alkyl bonds of CpCr(NO)$_2$R to give [CpCr(NO)$_2$(NR═O)][PF$_6$],[17] and Bergman and co-workers have observed intramolecular alkyl/nitrosyl migratory insertions in (η^5-C$_5$H$_5$)Co(NO)(R) complexes that give stable η^1-nitrosoalkane products (η^5-C$_5$H$_5$)Co(NR═O)(PPh$_3$) in the presence of trapping PPh$_3$.[18,19] The ^{1}H NMR spectrum of **6** shows a methyl resonance at δ 3.12, and ν_{NO} is observed at 1378 cm^{-1} in the IR spectrum, values similar to those observed for other coordinated nitrosoalkanes.[18] The methyl carbon of **6** resonates as a quartet at δ 88.5 in the ^{13}C NMR spectrum. The *trans*,*mer*-geometry for the phosphine and carbonyl ligands is maintained as indicated by the ^{31}P{^{1}H} NMR (singlet, δ 10.4) and IR spectra (ν_{CO} = 2078(w), 2001(s), 1967(s) cm^{-1}). As was observed in the reactions of **1** (eq 2), reaction of **5** with [NO][X] (X = PF$_6$, BF$_4$) resulted in the isolation of the fluoride complex **4**.



(3)



(4)

To assess whether the nitrosonium insertions were peculiar to this Re(I) system, we have investigated the reaction of a d^6 osmium hydride, *cis*,*trans*-OsHBr(CO)$_2$(PPh$_3$)$_2$ (**7**), with nitrosonium triflate (eq 4). The reaction affords a new nitroxyl complex [*cis*,*trans*-OsBr(NH═O)(CO)$_2$(PPh$_3$)$_2$][SO$_3$CF$_3$] (**4**) as orange crystals in 52% yield, which has been characterized by IR and NMR (^{1}H, ^{31}P) spectroscopy and elemental analysis.[14] The nitroxyl proton resonates at δ 20.70 in the ^{1}H NMR spectrum (CD$_2$Cl$_2$), and the ligand's ν_{NO} occurs at 1365 cm^{-1}, both typical for M−NH═O moieties. The ^{31}P{^{1}H} NMR shows a singlet for the trans-disposed phosphines at δ 2.7, and a cis orientation for the carbonyl ligands is indicated by two strong ν_{CO} at 2059 and 1998 cm^{-1} in the infrared. The IR and ^{31}P NMR data are similar to those found in the isoelectronic diazene complex [*cis*,*trans*-OsBr(NH═NH)(CO)$_2$(PPh$_3$)$_2$][SO$_3$CF$_3$] (ν_{CO} = 2061(s) and 2001(s) cm^{-1}; ^{31}P = δ −2.1) which has been crystallographically characterized.[13d]

In summary, insertion reactions of phenyldiazonium and nitrosonium salts with several hydride and alkyl complexes have been investigated. We observed that nitrosonium, like the related aryldiazonium ions, undergoes facile 1,1-insertions with d^6 hydrido and alkyl complexes to give new complexes containing nitroxyl and nitrosoalkane ligands, the stabilities of which are highly dependent on the nature of the nitrosonium salt used. Nitrosonium hexafluorophosphate and tetrafluoroborate salts yield thermally unstable complexes that decompose with ligand loss to the neutral fluorides, whereas nitrosonium triflate reacts to give the moderately stable salts [*mer*,*trans*-Re(NH═O)(CO)$_3$(PPh$_3$)$_2$][SO$_3$CF$_3$] (**3**), [*mer*,*trans*-Re{N(CH$_3$)═O}(CO)$_3$(PPh$_3$)$_2$][SO$_3$CF$_3$] (**6**), and [*cis*,*trans*-OsBr(NH═O)(CO)$_2$(PPh$_3$)$_2$][SO$_3$CF$_3$] (**8**). The related phenyldiazene salt [*mer*,*trans*-Re(CO)$_3$(NH═NPh)(PPh$_3$)$_2$][PF$_6$] (**2**) has also been prepared and crystallographically characterized.

Acknowledgment. We are grateful to the National Science Foundation and the Petroleum Research Fund, administered by the ACS, for financial support of this research through grants to G.L.H., and to the Department of Education for GAANN Fellowships to R.M. and J.S.S.

Supporting Information Available: Synthetic, spectroscopic, and analytical details (PDF); crystallographic details for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0277475