that would be inversely proportional to the concentration of the phosphine. However, as pointed out by Halpern and co-workers, the intercepts could be too small to be observed in the case of species, such as PPh_3, which are highly reactive toward the trapping of the intermediate. Our experiments thus may not distinguish between the two mechanisms. Our study[29] of the variation of k_2 with tertiary phosphine in the reaction of the phosphine with $[(\eta^5\text{-Cp})(CO)_2FeCH_2Cy]$ in DMSO, and of the variation of k_2/k_{-1} in the reaction of tertiary phosphine with $[(\eta^5\text{-Cp})(CO)_3MoCH_2Ph]$ in acetonitrile, showed a strongly decreasing k_2 with increasing cone angle of the phosphine but no correlation with the electronic parameter. We believe that significant steric discrimination would be unlikely if the intermediate were coordinatively unsaturated.

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Conclusions

Solvent-coordinated acyl complexes have been identified in the direct reactions of manganese alkyl complexes $[(CO)_5MnR]$ with polar solvents. Kinetic analysis of the reactions of $[(CO)_5MnCH_2C_6H_4Me\text{-}4]$ with PPh_3 in toluene, containing polar solvents or reaction promoters, is unable to distinguish whether the solvent-coordinated acyl complexes react directly with PPh_3 or whether prior dissociation of solvent takes place.

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Reactions of the Low-Valent Rhenium Oxo Anions $NaRe(O)(RC{\equiv}CR)_2$ with Alkyl and Aryl Halides; Evidence for both S_N2 and Radical Mechanisms[1]

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The low-valent monooxo compounds $NaRe(O)(RC{\equiv}CR)_2$ [R = Me (**1a**), Et (**1b**), Ph (**1c**)] are strong bases and potent reducing agents, highly unusual reactivity for terminal oxo compounds. They are all protonated by H_2O in CD_3CN, **1a** and **1b** even by stoichiometric acetone in this solvent, to form the Re(III) oxo hydride complexes $Re(O)H(RC{\equiv}CR)_2$. Compounds **1** react as nucleophiles with the Me^+ sources MeI, MeOTs, and $Me_3O^+BF_4^-$ and with the acyl sources acetic anhydride and acetyl chloride, forming $Re(O)Me(RC{\equiv}CR)_2$ and $Re(O)[C(O)Me](RC{\equiv}CR)_2$, respectively. While there is no evidence for radical intermediates with these reagents, reactions with primary to tertiary alkyl halides occur at least in part by an electron-transfer pathway. Primary and secondary alkyl halides react to form mixtures of Re(III) alkyls, $Re(O)R'(RC{\equiv}CR)_2$, and Re(II) dimers, $Re_2(O)_2(RC{\equiv}CR)_4$ (**2**). ^{t}BuI and **1** produce solely **2** and the organic radical disproportionation products isobutane and isobutylene. The intermediacy of organic radicals is confirmed by significant cyclization of the hexenyl radical clock in the reaction of 6-iodo-1-hexene with **1a**. Aryl halides are also reactive with **1a** and **1b** to produce, in roughly equal yields, novel $Re(O)Ph(RC{\equiv}CR)_2$ compounds and **2** in C_6D_6 solvent. In CH_3CN, however, trapping of aryl radicals by the solvent occurs to produce $Re(O)CH_2CN(RC{\equiv}CR)_2$ compounds and arene (together with **2**). These reactions appear to occur via initial electron transfer from rhenium to the organic halide. Compounds **1** are tightly ion paired and show reactivity that is dependent on the solvent and on the presence or absence of 15-crown-5. The diphenylacetylene derivative **1c** is significantly less reactive than the dialkylacetylene complexes **1a** and **1b** because of the influence of the better π acceptor $PhC{\equiv}CPh$ on the HOMO in **1**.

Transition metal-terminal oxo complexes are typically high-valent species and are widely used as reagents and catalysts in oxidation reactions.[4,5] We have recently isolated novel rhenium-oxo-bis(acetylene) anions, $NaRe(O)(RC{\equiv}CR)_2$ [R = Me (**1a**), R = Et (**1b**), R = Ph (**1c**)],[6] that are formally Re(I) and typically act as reductants.

Scheme I

Halogen Atom Abstraction

$$RX + M^n \longrightarrow R^\bullet + XM^{n+1}$$

Electron Transfer

$$RX + M^n \longrightarrow RX^{\bullet-} + M^{n+1}$$

Nucleophilic Attack

$$RX + M^n \longrightarrow RM^{n+2} + X^- \text{ or } RM^{n+2}X$$

This report describes the reactions of compounds **1** with alkyl and aryl halides, in order to better understand the unusual reactivity of these remarkable species.

Reactions of alkyl halides with transition-metal compounds have been extensively studied for their role in a variety of processes such as the synthesis of transition-metal alkyls,[7] the coupling reactions assisted by transition

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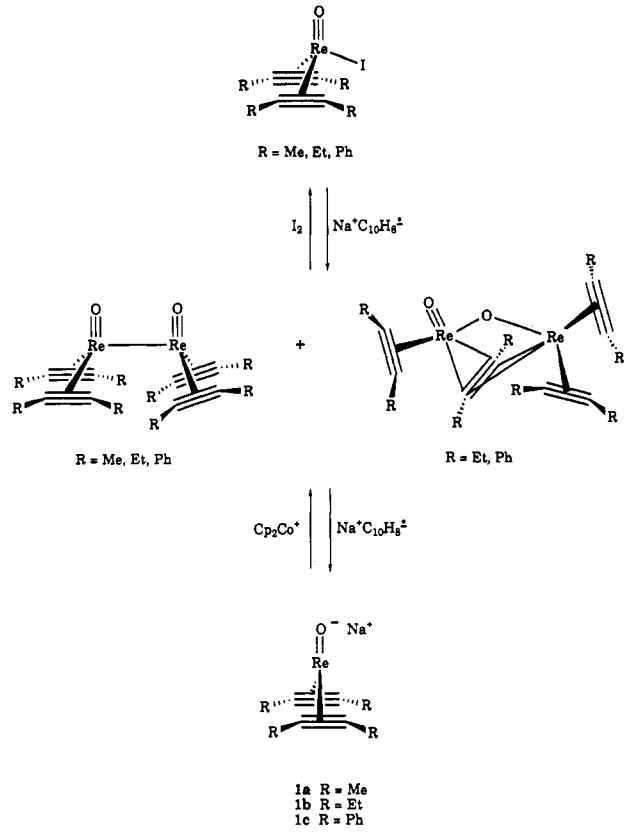
Scheme II



metals,[8] and the Monsanto acetic acid process.[9] These studies have amassed evidence for three types of mechanisms:[10-12] (i) halogen atom abstraction by the metal center, (ii) electron transfer from the metal to the alkyl halide, and (iii) nucleophilic attack of the metal on the alkyl carbon (Scheme I). The first two involve a one-electron change at the metal center, while the last is a two-electron process, usually described as an S_N2 mechanism.[12] We report here that, depending on the substrate, compounds 1 can react by either electron transfer or nucleophilic mechanisms.

Compounds 1 are prepared by reduction of rhenium(III)-oxo-iodide complexes, $Re(O)I(RC{\equiv}CR)_2$, either directly with 2 equiv of reducing agent or in one-electron steps through the Re(II) dimers $Re_2(O)_2(RC{\equiv}CR)_4$ (2) (Scheme II).[13] The dimers, which exist as both symmetric and asymmetric isomers (illustrated in Scheme II and described in detail elsewhere[13]), are also formed on one-electron oxidation of the anions 1, for instance by O_2, Cp_2Fe^+, or Cp_2Co^+.

Experimental Section

Syntheses were performed by using standard Schlenk or vacuum line techniques and a continuous nitrogen flow glovebox except as indicated. Solvents and reagents were dried and deoxygenated by standard methods[14] (unless otherwise mentioned). Reactions were executed at ambient temperatures unless otherwise stated. NMR spectra were obtained on Varian VXR-300 and Bruker WM-500 spectrometers. ^1H chemical shifts are reported in ppm downfield from Me_4Si: δ (number of hydrogens, multiplicity, coupling constant, assignment) and ^{13}C chemical shifts were referenced to solvent peaks (CD_3CN, 0.5 ppm; CD_2Cl_2, 55.0 ppm; C_6D_6, 128.7 ppm). IR spectra were obtained on NaCl plates with Perkin-Elmer 283 and FT 1604 spectrometers and are reported in inverse centimeters. Elemental analyses were performed by Canadian Microanalytical (Delta, British Columbia). Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS instrument using the direct inlet method with a 70-eV ionizing radiation if M^+ is reported. Alternately, if $[M + H]^+$ is listed, the spectrum was a FAB-MS acquired by using a VG 70 SEQ tandem hybrid instrument of EBqQ geometry (VG Analytical, Altrincham, U.K.). The instrument was equipped with a standard unheated VG FAB ion source and a standard saddlefield gun (Ion Tech Ltd., Middlesex, U.K.) producing a beam of xenon atoms at 8 keV and 1 mA. The mass spectrometer was adjusted to a resolving power of 1000 and spectra were obtained at 8 kV and at a scan speed of 10 sec/decade. 3-Nitrobenzylalcohol was used as the matrix in the positive ion FAB-MS mode.

Compounds 1,[6] $Re_2(O)_2(RC{\equiv}CR)_4$ (2),[13] $Re(O)Me(RC{\equiv}CR)_2$ (3) (R = Me, Et),[15] $Re(O)I(RC{\equiv}CR)_2$ (4) (R = Me, Et),[16] $Re(O)H(RC{\equiv}CR)_2$ (R = Me, Et),[15] $Re(O)Et(RC{\equiv}CR)_2$ (R = Me, Et),[15] $Re(O)\eta^1$-allyl$(MeC{\equiv}CMe)_2$,[15] $Re(O)^iPr(RC{\equiv}CR)_2$ (R = Me, Et),[15] and $Re(O)(I)_3(PPh_3)_2$[17] have been previously reported. Anhydrous $ZnCl_2$ was prepared by treatment of $ZnCl_2$ (Baker) with thionyl chloride;[18] (cyclopentylmethyl)iodide was synthesized from cyclopentylmethanol (Aldrich) and PI_3 (Strem) similar to literature methods;[19] 6-iodo-1-hexene was prepared via the Finkelstein reaction[20] using 6-bromo-1-hexene (Aldrich); and sodium naphthalenide solutions (NaC_8H_{10}) were prepared by literature methods.[21] The following reagents were used as received: $PhC{\equiv}CPh$ (Farchan); 97% $^{18}OH_2$ (Cambridge Isotope Laboratories); MeLi, 1.4 M in Et_2O (Aldrich); PhLi, 1.7 M in 70/30 hexane/Et_2O (Aldrich); and PhI (Aldrich).

The reactions were typically carried out by charging an NMR tube with 10–15 mg of 1 and 0.3–0.4 mL of C_6D_6 or CD_3CN and then adding 1–2 equiv of the reactant and characterizing the products by comparison to NMR and mass spectra of authentic samples. Novel $Re(O)R'(RC{\equiv}CR)_2$ products were identified by analogy to known species and were characterized by their ^1H NMR and mass spectra.

$Re(O)Me(PhC{\equiv}CPh)_2$ (3c). $Re(O)I(PhC{\equiv}CPh)_2$, **4c** (0.200 g, 0.29 mmol), and 20 mL of C_6H_6 were combined, and the solution was cooled to 0 °C. To $ZnCl_2$, 0.056 g (0.41 mmol), was added 10 mL of Et_2O and 0.40 mL of MeLi (0.56 mmol) at −78 °C. This solution was warmed to 0 °C for a 0.5 h while being stirred; then it was cooled to −78 °C and syringed onto the frozen C_6H_6 solution

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above. It was allowed to warm to room temperature and stirred 1 h, and the solvent was removed. A toluene and silica gel slurry (5 mL) was added and the resulting mixture filtered and washed with more toluene. The toluene was removed in vacuo to yield 0.117 g (0.20 mmol, 67%) of very light yellow solids, which were washed with CH_3CN. ^1H NMR (C_6D_6): 7.48 (4 H, d, 8 Hz), 7.30 (4 H, m), 7.13 (4 H, t, 8 Hz), 7.02 (2 H, t, 8 Hz), 6.93 (6 H, m) (C_6H_5); 2.88 (3 H, s, $ReCH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 149.4, 146.5 ($PhC{\equiv}C'Ph$); 131.1, 128.8, 127.1, 126.3, 125.8, 125.4, 125.6, 124.9 (C_6H_5); 11.9 ($Re{-}CH_3$). IR (Nujol): 1770 [ν(C≡C)], 1593, 1572, 1026, 999, 961 (s) [ν(Re=O)], 923, 695, 768, 742, 630, 620, 599, 517, 500, 460. MS: m/z 574/572 $(M)^+$. Anal. Calcd for $C_{29}H_{23}ReO$: C, 60.71; H, 4.04. Found: C, 60.30; H, 4.06.

Re(O)I(PhC≡CPh)$_2$ (4c). $Re(O)(I)_3(PPh_3)_2$ (4 g), PhC≡CPh (2.9 g, 17 mmol), and 2 mL of H_2O were combined on the benchtop, and the solution was stirred in 75 mL of C_6H_6/CH_2Cl_2 (1:1) for 72 h. After stripping to dryness, 3:2 EtOAc/hexanes was added and the solution filtered through a silica gel plug and washed with the EtOAc/hexane mixture until the filtrate was no longer colored. The filtrate was concentrated and loaded on a silica gel column. The organics were removed with hexanes and the orange-yellow product eluted with 1:4 EtOAc/hexanes to afford, after solvent removal in vacuo, 1.11 g of **4c** (70% based on $KReO_4$). The 75% ^{18}O-labeled compound was prepared by stirring **4c** in THF with 10 equiv of $^{18}OH_2$ for 2 days and again in CH_2Cl_2 with 7 equiv of $^{18}OH_2$ for 2 days. ^1H NMR (C_6D_6): 7.88 (4 H, d, 7 Hz), 7.16 (4 H, t, 8 Hz), 7.05 (4 H, d, 7 Hz), 7.01 (2 H, t, 8 Hz), 6.82 (6 H, m) (C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 147.6, 144.7 ($PhC{\equiv}C'Ph$); 133.4, 132.1, 132.2, 129.8, 128.4, 130.3, 129.4 (C_6H_5). IR (Nujol): 1732 [ν(C≡C)], 1604 (w), 1274, 1156, 1070, 1026, 972 (s) [ν(Re=O)] {ν(Re=^{18}O) 920}, 762, 754, 740, 722, 690, 668. MS: m/z 686/684 $(M)^+$, 559/557 $(M-I)^+$, 508/506 $(M-PhC{\equiv}CPh)^+$. Anal. Calcd for $C_{28}H_{20}ReOI$: C, 49.05; H, 2.94. Found: C, 49.11; H, 2.89.

Re(O)H(PhC≡CPh)$_2$. To **4c**, 0.207 g (0.30 mmol), and 25 mL of C_6D_6 was added 120 μL (0.45 mmol) of $^nBu_3SnH$. The solution was stirred for 0.5 h, turning from orange-yellow to cream color, and the solvent was removed in vacuo. Et_2O (20 mL) was added and the solution stirred while the solvent was slowly distilled away, until about 5 mL was left and solids had precipitated. The off-white solids were filtered and washed once with Et_2O to yield 98 mg (0.18 mmol, 58%) of Re(O)H(PhC≡CPh)$_2$. ^1H NMR (C_6D_6): 7.83 (1 H, s) ($Re{-}H$); 8.12 (4 H, d, 8 Hz), 7.31 (4 H, m), 7.04–7.19 (6 H, m), 6.19 (6 H, m) (C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 151.6, 148.1 ($PhC{\equiv}C'Ph$); 135.2, 133.5, 133.3, 130.6, 131.4, 130.2, 130.2, 129.5 (C_6H_5). IR (Nujol): 3053 (w), 2038 (w) [ν(Re–H)], 1770 (w) [ν(C≡C)], 1442 (s), 1280, 1073, 961 (s) [ν(Re=O)], 926, 914, 762 (s), 690 (s). MS: 560/558 $(M)^+$. Anal. Calcd for $C_{28}H_{21}ReO$: C, 60.09; H, 3.78. Found: C, 59.88; H, 3.85.

Re(O)(η^1-allyl)(PhC≡CPh)$_2$. To a stirred solution of **4c** (0.105 g, 0.15 mmol) in 25 mL of THF at −78 °C was added 0.44 mL of a 0.73 M solution of $Na/C_{10}H_8$ in THF (0.32 mmol). To the resulting purple solution was added 21 μL of allyl iodide (0.23 mmol), and the reaction turned light tan. Removal of the solvent in vacuo followed by purification on silica gel (hexanes to remove the naphthalene followed by 1:4 EtOAc/hexanes to elute the Re(O)(η^1-allyl)(PhC≡CPh)$_2$) gave 83 mg (90%) of white fluffy solids, which were washed with CH_3CN. ^1H NMR (C_6D_6): 7.56 (4 H, d, 8 Hz), 7.25 (4 H, m), 7.17 (4 H, t, 8 Hz), 7.05 (2 H, t, 8 Hz), 6.97 (6 H, m) (C_6H_5); 5.22 (1 H, m) ($CH_2CH{=}CHH'$); 5.09 (2 H, t, 8 Hz) ($CH_2CH{=}CHH'$); 4.06 (1 H, dd, 8 Hz) ($CH_2CH{=}CHH'$); 4.03 (1 H, dd, 2 & 16 Hz) ($CH_2CH{=}CHH'$). $^{13}C\{^1H\}$ NMR (C_6D_6): 154.8, 149.6 ($PhC{\equiv}C'Ph$); 139.8 ($ReCH_2CH{=}CH_2$); 134.9, 132.5, 130.9, 129.9, 129.2, 128.8 (C_6H_5); 112.3 ($ReCH_2CH{=}CH_2$); 35.8 ($ReCH_2CH{=}CH_2$). IR (Nujol): 1760 (w) [ν(C≡C)], 1620, 1570 (w), 1265 (w), 1230 (w), 1075, 1028, 960 (s) [ν(Re=O)], 935 (w), 920 (w), 905 (w), 780, 749, 700. MS: 420/418 $(M^+ - PhC{\equiv}CPh)$; 379/377 $(M^+ - PhC{\equiv}CPh$ and $C_3H_5)$; no molecular ion was observed. Anal. Calcd for $C_{31}H_{25}ReO$: C, 62.08; H, 4.20. Found: C, 61.84; H, 4.32.

Re(O)[C(O)Me](MeC≡CMe)$_2$ (7a). To a stirred solution of **4** (0.20 g, 0.46 mmol) in 20 mL of THF at −78 °C was added 3.1 mL of a 0.30 M solution of $Na/C_{10}H_8$ in THF (2.0 equiv to **4**). To the resulting deep orange solution was added 58 μL of acetic anhydride (0.56 mmol), and the reaction immediately turned light tan. Removal of the solvent in vacuo followed by purification on silica gel (1:9 EtOAc/hexanes) gave 160 mg of **7a** (98%) as colorless solids. ^1H NMR (CD_3CN): 3.11 (3 H, s) ($ReC(O)CH_3$); 2.39, 2.34 (6 H each, q, 1 Hz) ($CH_3C{\equiv}CCH'_3$). ^{13}C NMR (C_6D_6): 248.8 (s) ($ReC(O)CH_3$); 143.1, 141.2 (both s) ($C{\equiv}C'$); 49.6 (q, 128 Hz) ($ReC(O)CH_3$); 15.3, 12.0 (both q, 129 Hz) ($CH_3C{\equiv}CC'H_3$). IR (neat): 2950, 2910, 2848, 1788 [ν(C≡C)], 1644 (s) [ν(C=O)], 1435, 1362, 1329, 1152, 1090, 1050, 952 (s) [ν(Re=O)], 890, 808 (w), 800 (w). MS: 354/352 $(M)^+$. Anal. Calcd for $C_{10}H_{15}ReO_2$: C, 33.98; H, 4.28. Found: C, 34.26; H, 4.23.

Re(O)Ph(MeC≡CMe)$_2$ (8a). This compound was prepared by using 0.249 g (0.57 mmol) **4a** and alkylzinc reagents ($ZnCl_2$, 0.110 g, 0.81 mmol; PhLi, 0.64 mL, 1.1 mmol) analogous to Re(O)Me(PhC≡CPh)$_2$ above. The yield of very light cream solids was 0.149 g (0.39 mmol, 68%). Further purification was accomplished by sublimation at 40 °C, 10^{-3} Torr. ^1H NMR (C_6D_6): 7.23 (2 H, t), 7.02 (3 H, m) (C_6H_5); 2.12, 2.54 (6 H each, q, 1 Hz) ($CH_3C{\equiv}CCH'_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 167.5 (C_{ipso}); 148.6, 144.1 ($C{\equiv}C'$); 136.0, 130.2 (C_{ortho} and C_{meta}); 124.2 (C_{para}); 17.3, 12.5 ($CH_3C{\equiv}CC'H_3$). IR (Nujol): 3058, 3036, 1790 (w) [ν(C≡C)], 1572, 1158, 1020, 953 (s) [ν(Re=O)], 735 (s), 705, 654. MS: 389/387 $[M+H]^+$. Anal. Calcd for $C_{14}H_{17}ReO$: C, 43.30; H, 4.42. Found: C, 43.44; H, 4.45.

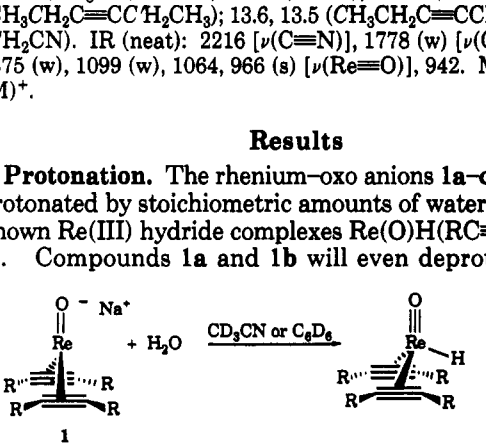
Re(O)Ph(EtC≡CEt)$_2$ (8b). Synthesis was performed analogous to **8a** by using 0.195 g (0.40 mmol) of **4b**, 0.061 g (0.45 mmol) of $ZnCl_2$, and 0.44 mL of PhLi solution (0.76 mmol). Yield was 0.162 g (0.37 mmol, 92%) of a light green-yellow oil. ^1H NMR (C_6D_6): 7.29 (3 H, m), 7.08 (2 H, t), (C_6H_5); 3.12, 3.02, 2.77, 2.51 (2 H each, m) ($CH_3CHH'C{\equiv}CCH'H''CH_3$); 1.24, 0.98 (6 H each, t, 8 Hz) ($CH_3CH_2C{\equiv}CCH_2CH'_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): 166.5 (C_{ipso}); 151.9, 144.1 ($C{\equiv}C'$); 136.0, 129.9 (C_{ortho} and C_{meta}); 124.0 (C_{para}); 25.9, 21.5 ($CH_3CH_2C{\equiv}CC'H_2CH_3$); 15.3, 15.1 ($CH_3CH_2C{\equiv}CCH_2C'H_3$). IR (neat): 3056, 1777 (w) [ν(C≡C)], 1574, 1455 (s), 1373, 1305, 1060, 963 (s) [ν(Re=O)], 731 (s), 700. MS: 444/442 $[M+H]^+$.

Re(O)CH$_2$CN(MeC≡CMe)$_2$ (9a). Synthesis was accomplished by addition of 50 μL (0.45 mmol) of PhI to **1a** (0.114 g, 0.34 mmol) in 15 mL of CH_3CN, filtration, and removal of the solvent in vacuo. ^1H NMR of the residue shows ~60% **9a** and 40% **2a**; however, sublimation at 35–40 °C, 10^{-3} Torr results in an isolated yield of only 15 mg (0.043 mmol, 13%) of compound **9a**, a light cream oil (the heating causes much decomposition). ^1H NMR (CD_3CN): 3.55 (2 H, s) (CH_2CN); 3.01, 2.62 (6 H each, q, 1 Hz) ($CH_3C{\equiv}CCH'_3$). $^{13}C\{^1H\}$ NMR (CD_3CN): 143.9, 143.1 ($C{\equiv}C'$); 125.7 ($C{\equiv}N$); 14.8, 8.9 ($CH_3C{\equiv}CC'H_3$); −3.8 (CH_2CN). IR (neat): 2215 [ν(C≡N)], 1790 (w) [ν(C≡C)], 1644, 1601, 1434, 1366, 1158, 1044, 959 (s) [ν(Re=O)]. MS: 351/349 $(M)^+$.

Re(O)CH$_2$CN(EtC≡CEt)$_2$ (9b). Synthesis of compound **9b** was similar to that for **9a**, using **1b**; sublimation at 45–50 °C gives **9b**, a light cream oil. ^1H NMR (CD_3CN): 3.59 (2 H, s) (CH_2CN); 3.53, 3.30, 3.06, 3.07 (2 H each, m) ($CH_3CHH'C{\equiv}CH'H'''CH_3$); 1.42, 1.30 (6 H each, t, 8 Hz) ($CH_3CH_2C{\equiv}CCH_2CH'_3$). $^{13}C\{^1H\}$ NMR (CD_3CN): 148.0, 146.7 ($C{\equiv}C'$); 126.0 ($C{\equiv}N$); 24.0, 18.9 ($CH_3CH_2C{\equiv}CC'H_2CH_3$); 13.6, 13.5 ($CH_3CH_2C{\equiv}CCH_2C'H_3$); −5.1 ($CH_2CN$). IR (neat): 2216 [$\nu$(C≡N)], 1778 (w) [$\nu$(C≡C)], 1456, 1375 (w), 1099 (w), 1064, 966 (s) [ν(Re=O)], 942. MS: 409/407 $(M)^+$.

Results

Protonation. The rhenium–oxo anions **1a–c** are rapidly protonated by stoichiometric amounts of water to form the known Re(III) hydride complexes Re(O)H(RC≡CR)$_2$[15] (eq 1). Compounds **1a** and **1b** will even deprotonate stoi-



chiometric acetone in acetonitrile solvent, but are stable in acetonitrile alone; **1c** is unreactive toward acetone. The diphenylacetylene hydride can be deprotonated back to **1c** by $Na[N(SiMe_3)_2]$ in C_6D_6.

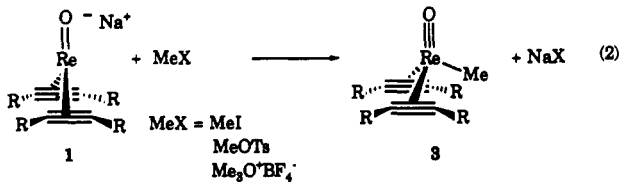
Reactions with Alkyl Halides. Compounds **1** react with methyl iodide within time of mixing to form the

Table I. Reactions of Alkyl and Aryl Halides with 1a–c

reagents			% Re(O)R′(RCCR)$_2$	% Re$_2$(O)$_2$(RCCR)$_4$[a]	organic products[b]
MeI	1b	C_6D_6	100		
MeI	1b	CD_3CN	100		
EtI	1a	C_6D_6	86	14	
EtI	1a	CD_3CN	80	20	
EtI	1c	C_6D_6	51	49 (2:3)	
^{i}PrI	1a	C_6D_6	38	62	$Me_2CHCHMe_2$
^{i}PrI	1a	CD_3CN	35	65	$Me_2CHCHMe_2$
^{i}PrI	1b	CD_3CN	10	90 (4:1)	$Me_2CHCHMe_2$
^{i}PrI	1c	C_6D_6		100 (1:1)	$Me_2CHCHMe_2$
^{t}BuI	1b	CD_3CN		100 (10:1)	$Me_2C{=}CH_2$ + Me_3CH (1:1)
^{t}BuI	1c	C_6D_6		100 (3:2)	$Me_2C{=}CH_2$ + Me_3CH (1:1)
^{t}BuI	1c	CD_3CN		100[c]	$Me_2C{=}CH_2$ + Me_3CH (1:1)
(allyl)I	1b	C_6D_6	53	47[d]	
(allyl)I	1b	CD_3CN	30	70 (9:1)	
(allyl)I	1c	C_6D_6	70	30 (3:2)	
$PhCH_2Br$	1a	C_6D_6	65	35	$PhCH_2CH_2Ph$
$PhCH_2Br$	1a	CD_3CN	20	80	$PhCH_2CH_2Ph$[h]
$PhCH_2Br$	1c	C_6D_6	59	41 (2:3)	$PhCH_2CH_2Ph$
$CH_2{=}CH(CH_2)_4I$	1a	C_6D_6	41[e] 44[f]	15	
$CH_2{=}CH(CH_2)_4I$	1a	CD_3CN	55[e] 25[f]	20	
$C_5H_9CH_2I$	1a	C_6D_6	51[i]	15[i]	
$C_5H_9CH_2I$	1a	CD_3CN	55[i]	32[i]	
$(CH_2)_5CHBr$	1a	C_6D_6	68	32	
$(CH_2)_5CHBr$	1a	CD_3CN	85	15	
$NCCH_2I$	1a	CD_3CN	50	50	
PhI	1a	C_6D_6	62	38	
PhI	1a	CD_3CN	64[g]	36	
PhI	1b	C_6D_6	57	43[d]	
PhI	1b	CD_3CN	60[g]	40 (5:1)	
p-TolI	1b	C_6D_6	53	47[d]	
p-TolI	1b	CD_3CN	70[g]	30[d]	*p*-$CH_3C_6H_4D$

[a] Combined yield of symmetric and asymmetric dimers; their ratio is given in parentheses. [b] Major organic products observed by NMR spectroscopy. Organic products were not determined in all cases. [c] Ratio not determined because of the insolubility of one of the Re$_2$(O)$_2$(PhCCPh)$_4$ isomers in CD_3CN. [d] Asymmetric dimers not observed. [e] R′ = 5-hexenyl. [f] R′ = cyclopentylmethyl. [g] R′ = CD_2CN. [h] An unidentified organic product is also seen. [i] An unidentified metal product is also observed, possibly from a contaminant in the alkyl halide reagent.

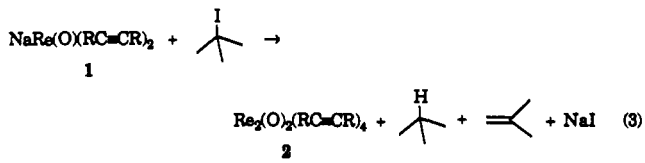
Re(III) oxo methyl complexes, Re(O)Me(RC≡CR)$_2$ (3) (eq 2; Table I).[15] The methyl complexes have been previously



(2)

prepared by alkylation of Re(O)I(RC≡CR)$_2$ (4) with $ZnMe_2$.[15] As in the protonation reactions, clean oxidation of Re(I) to Re(III) is observed both in benzene and in acetonitrile, without any formation of the dimers **2**. Alkylation with the harder Me^+ sources MeOTs and $Me_3O^+BF_4^-$ should be more likely to occur at oxygen, by analogy with alkylations of organic anions such as enolates,[22] but these reagents also yield solely **3**. Similarly, no intermediates are observed on protonation of **1b** at −78 °C in THF. The only reactions of **1** in which attack at oxygen has been observed are those with silicon Lewis acids, such as Me_3SiCl, to give the rhenium(I) siloxide complexes Re(OSiMe$_3$)(RC≡CR)$_3$ (R = Me, Et).[23] At −30 °C in CD_3CN, **1c** and MeI instantly produce **3c**, without evidence for any intermediate, even in the presence of 2-butyne to trap a species such as Re(OMe)(RC≡CR)$_3$. Similarly, no intermediates are observed on protonation of **1b** with $MeC_6H_4SO_3H$ at −78 °C in THF.

In contrast, ^{t}BuI reacts with compounds **1** to form the rhenium(II) dimers **2** as the sole metal products (by ^{1}H NMR analysis), plus isobutylene and isobutane (eq 3; Table I). Rhenium(III)–*tert*-butyl complexes analogous



(3)

to **3** have not been observed. Likewise, alkylation of Re(O)I(RC≡CR)$_2$ (**4**) with *tert*-butyl zinc reagents—a route successful for methyl, ethyl, and isopropyl derivatives[15]—yields only the dimers **2**; it is clearly difficult to generate the ^{t}Bu derivatives in this system. Both the symmetric and asymmetric isomers of **2** are formed.[13] For instance, reaction of **1b** with ^{t}BuI in CD_3CN yields a 10:1 ratio of symmetric to asymmetric dimers; in C_6D_6, **1c** + ^{t}BuI gives a 3:2 ratio. The formation of isobutane and isobutylene in roughly equal yields is suggestive of a radical process, since these are the predominant products of ^{t}Bu radical disproportionation.[24] Similarly, generation of the rhenium(II) radical Re(O)(RC≡CR)$_2$• should lead to dimers.[13b]

The reactivity of primary and secondary alkyl halides is intermediate between MeI and ^{t}BuI, as both Re(III)–

(22) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*; 3rd ed.; Wiley-Interscience: New York, 1985; pp 322–325. Similar metal versus ligand alkylations are reported in: Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1285–1299. Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099–4100.

(23) Reference 6 and R. R. Conry, unpublished results. The reaction of **1c** with Re(O)I(MeC≡CMe)$_2$ may also proceed by initial attack at the oxo of **1c**.[13b]

(24) Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441–464.

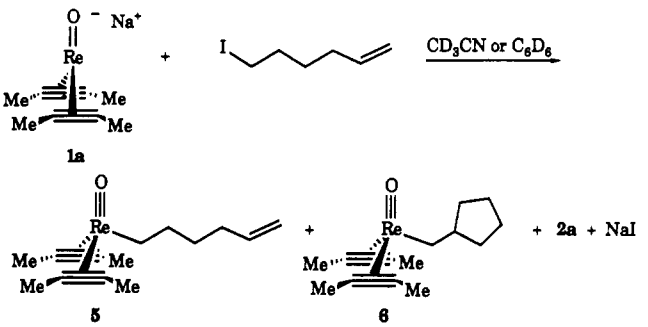
oxo–alkyl complexes and dimers are formed (eq 4), as given in Table I. ^{i}PrI reacts immediately with **1a** in C_6D_6 or

$$\underset{\mathbf{1}}{NaRe(O)(RC{\equiv}CR)_2} + R'X \rightarrow Re(O)R'(RC{\equiv}CR)_2 + \underset{\mathbf{2}}{Re_2(O)_2(RC{\equiv}CR)_4} + NaX + \text{organic products} \quad (4)$$

R′X = EtI, $PhCH_2Br$, $CH_2{=}CHCH_2I$, ^{i}PrI, cyclohexyl bromide, cyclopentylmethyl iodide

CD_3CN to give a 1:2 mixture of $Re(O)^{i}Pr(MeC{\equiv}CMe)_2$ and the dimer $Re_2(O)_2(MeC{\equiv}CMe)_4$ (**2a**). The same products are obtained on alkylation of $Re(O)I(MeC{\equiv}CMe)_2$ with $^{i}Pr_2Zn$.[15] 2,3-Dimethylbutane, the product from coupling of two isopropyl radicals, is observed by ^{1}H NMR spectroscopy. Similarly, the reaction of benzyl bromide and **1a** in C_6D_6 yields 65% $Re(O)(CH_2Ph)(MeC{\equiv}CMe)_2$ and 35% **2a**. Bibenzyl is also formed, in a 1:1 ratio with **2a**.

Reaction of **1a** and 6-iodo-1-hexene yields **2a** and two rhenium(III)–oxo–alkyl complexes (by ^{1}H NMR analysis), both the 5-hexenyl (**5**) and cyclopentylmethyl (**6**) derivatives (eq 5). The cyclopentylmethyl complex **6** can also

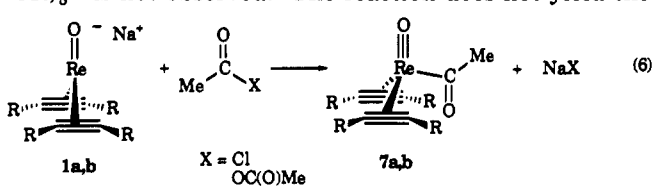


(5)

be prepared from **1a** and *c*-$C_5H_9CH_2I$. The cyclopentylmethyl fragment arises from cyclization of the 5-hexenyl radical, a well-known radical clock.[25] The ratio of **5** to **6** is sensitive to solvent and concentration: in C_6D_6, roughly equal amounts of **5** and **6** are formed (41% **5**, 44% **6**, 15% **2a**), while in CD_3CN under similar conditions **5** predominates (55% **5**, 25% **6**, 20% **2a**). The same reaction in acetonitrile but 10 times more dilute (2×10^{-3} M) yielded more of the cyclized product and of the dimer (20% **5**, 40% **6**, and 40% **2a**), consistent with cyclization of the radical clock being competitive with radical recombination.

In all of these reactions of **1** with simple alkyl halides, there is no evidence for the formation of rhenium–halide complexes such as **4**. The trihalomethanes iodoform and chloroform do, however, yield $Re(O)X(RC{\equiv}CR)_2$ [X = I (**4**), Cl]. For instance, **1a** reacts with CHI_3 to give roughly a 50/50 mixture of **4a** and the dimers **2a** in both benzene and acetonitrile solvents. CHI_3 and $CHCl_3$ are good halogen atom donors as well as electron acceptors, so presumably the rhenium halides are formed by their trapping the Re(II) radical.

The anions **1a,b** are also rapidly acylated by acetic anhydride or acetyl chloride (eq 6). Addition to the oxo group to form the stable acetate complex $Re[OC(O)Me](RC{\equiv}CR)_3$[26] is not observed. The reaction does not yield the

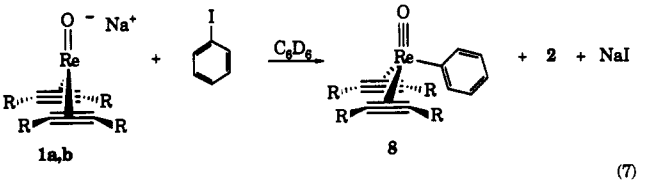


(6)

(25) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317–323.

acetate even in the presence of added acetylene or acetylene and 15-crown-5. The novel acyl complex **7a** has been characterized by NMR and IR spectroscopies (ν_{CO} = 1648 cm^{-1}), mass spectrometry, and elemental analysis. Like the reactions with methyl sources, dimers are not formed in the acylation reactions.

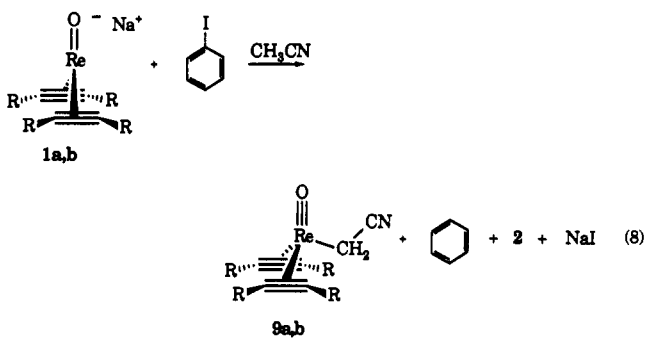
Aryl Halides. Compounds **1a** and **1b** react rapidly with iodobenzene, while the diphenylacetylene derivative **1c** is unreactive over 2 days at ambient temperatures. In C_6D_6 solvent, **1a** or **1b** with PhI gives dimers (40%) and the previously unknown Re(III)–oxo–phenyl complex $Re(O)Ph(RC{\equiv}CR)_2$ (roughly 60%; R = Me (**8a**), Et (**8b**); eq 7).



(7)

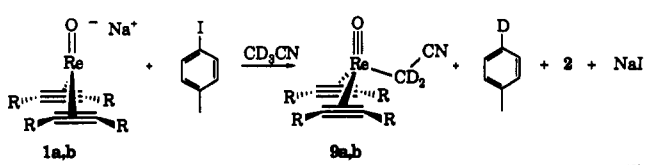
Compounds **8** can also be isolated from alkylation of $Re(O)I(RC{\equiv}CR)_2$ (**4**) with diphenylzinc (see Experimental Section), and they have been fully characterized. When prepared in C_6D_6, there is no incorporation of deuterium in the Re–aryl group (by ^{1}H NMR and mass spectrometry).

In CH_3CN solvent, however, reaction of **1a** or **1b** with PhI does not give **8**. Instead, a cyanomethyl complex, $Re(O)CH_2CN(RC{\equiv}CR)_2$ (**9**), is formed, in about 60% yield (by ^{1}H NMR analysis), along with dimers and benzene (eq 8). The identification of **9a** and **9b** as cyanomethyl com-



(8)

plexes is based on parent ions in their mass spectra and spectroscopic data, including APT ^{13}C NMR spectroscopy.[27] For **9a**, the CH_2CN group exhibits an IR band at 2215 cm^{-1} (C≡N), a resonance at δ 3.55 in the ^{1}H NMR spectrum ($CH_2C{\equiv}N$), and resonances at δ 125.7 and −3.8 in its ^{13}C NMR spectrum ($CH_2C{\equiv}N$, $CH_2C{\equiv}N$). In addition, **9a** is also the product of the reaction of **1a** and ICH_2CN, together with an equal amount of the dimers **2**. Other examples of cyanomethyl complexes are known.[28] Using CD_3CN as the solvent results in formation of **9**-d_2 (by ^{1}H NMR and mass spectrometry, e.g. eq 9), which



(9)

(26) See ref 16 in: Conry, R. R. Ph.D. Thesis, University of Washington, 1991.

(27) Yoder, C. H.; Schaeffer, C. D., Jr. *Introduction to Multinuclear NMR*; Benjamin/Cummings: Menlo Park, CA, 1987; p 199.

(28) For instance: Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 1999. Sostero, S.; Traverso, O.; Ros, R.; Michelin, R. A. *J. Organomet. Chem.* **1983**, *246*, 325. Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4103–4104.

shows that the solvent is the source of the cyanomethyl fragment. Reactions with *p*-iodotoluene in CD_3CN yield *p*-toluene-d_1 (eq 9), which is readily identified by the simple AA'BB' pattern for the aromatic resonances in its ^1H NMR spectrum.

These results indicate that the reactions in acetonitrile generate aryl radicals, which subsequently abstract a hydrogen (or deuterium) atom from the solvent.[29] Coupling of rhenium and acetonitrilo radicals yields **9**. We have tried to intercept radicals with traps other than acetonitrile, although the reactivity of **1** limits the choices to traps that have very low acidity and are difficult to reduce. The rhenium radicals can be in part trapped by $^nBu_3SnH$: reaction of **1b** and PhI in CD_3CN in the presence of roughly 10 equiv of the tin hydride yields 10–15% $Re(O)H(EtC{\equiv}CEt)_2$.

Bromo-, chloro-, and even fluorobenzene react with **1a** and **1b** in CD_3CN to give roughly the same mix of products as observed for iodobenzene. The rates of these reactions are quite sensitive to the halide, with reactions occurring within the time of mixing for PhI, in 15 min for PhBr, 2 days for PhCl, and 5 days for PhF.

Discussion

The rhenium–oxo anions **1** are strong bases, capable of deprotonating water in acetonitrile, which has a pK_a of 30[30] (and **1a** and **1b** will even deprotonate acetone in this solvent). These anions are more basic than all of the metal carbonyl anions whose pK_a's have been studied quantitatively. $HRe(CO)_5$ and $CpW(CO)_2(PMe_3)H$, two of the weakest acids studied by Norton et al., have pK_a values of 21 and 26 in CH_3CN.[31] The rhenium anions **1** also appear to be good nucleophiles, for instance reacting with acetic anhydride to form acyl complexes. No dimers are formed in the reactions of **1** with proton, methyl, or acyl sources, suggesting that these occur by a nucleophilic (S_N2) pathway rather than a radical one. The presence of a highly nucleophilic metal center is remarkable and unprecedented in a metal–oxo complex.

Radicals do, however, appear to be involved in reactions of other alkyl and aryl halides with **1**. Reactions of ^iPrI yield $Me_2CHCHMe_2$, formed by combination of two isopropyl radicals, and ^tBuI gives isobutylene + isobutane, the typical products of disproportionation of $^tBu^{\bullet}$.[24] Cyclization of 5-hexenyl compounds to cyclopentylmethyl derivatives is a fingerprint of a radical process. Similarly, the production of arene and cyanomethyl complexes from aryl halides indicates the involvement of aryl radicals (*p*-tolyl radical + $CD_3CN \rightarrow MeC_6H_4D + {}^{\bullet}CD_2CN$).[32,33] Observation of the rhenium cyanomethyl and cyclopentylmethyl complexes **6** and **9** indicates that there is a rhenium species that can intercept alkyl radicals to form alkyl complexes, most likely the rhenium radical $Re(O)(RC{\equiv}CR)_2{}^{\bullet}$. This is also suggested by its trapping by $^nBu_3SnH$ to form $Re(O)H(RC{\equiv}CR)_2$. Generation of the rhenium radical $Re(O)(RC{\equiv}CR)_2{}^{\bullet}$ is known to lead to the dimers **2**,[13b] which are coproducts in all the reactions that involve alkyl and aryl radicals.

There are two common mechanisms for the formation of radicals in such oxidative addition processes: electron transfer from metal to RX and halogen atom abstraction by the metal (Scheme I). The data for this system are most consistent with an electron-transfer pathway (Scheme III).

Scheme III

$$\underset{\mathbf{1}}{NaRe(O)(RC{\equiv}CR)_2} + RX \rightarrow \{Na^+, Re(O)(RC{\equiv}CR)_2{}^{\bullet}, RX^{\bullet-}\} \rightarrow NaX + Re(O)(RC{\equiv}CR)_2{}^{\bullet} + R^{\bullet} \rightarrow \underset{\mathbf{2}}{Re_2(O)_2(RC{\equiv}CR)_4} + Re(O)R(RC{\equiv}CR)_2 + R_2 + RH + R(-H)$$

Halogen atom abstraction by **1** is less likely because the rhenium(II) halide radical anion, $[Re(O)I(RC{\equiv}CR)_2]^{\bullet-}$ is unstable: electrochemical reduction of **4** is irreversible, leading rapidly to I^- and dimers.[34,35] Fluorine atom abstraction from fluorobenzene is particularly difficult because of the strength of the C–F bond. An electron-transfer pathway is reasonable because compounds **1** are strong reducing agents, as shown by their reduction of Cp_2Co^+ to Cp_2Co. Electron transfer to alkyl and aryl halides (as indicated in Scheme III) is known to rapidly form the alkyl or aryl radical and X^-, even for fluorobenzene.[36]

The formation of aryl and alkyl radicals by electron transfer has been previously demonstrated in oxidative addition reactions of $Ni(PR_3)_3$ species,[12] and similar overall mechanisms have been suggested for the additions of alkyl halides to $CpFe(CO)_2^-$ and $Mo(CO)_2(dmpe)_2$.[37] The iron and molybdenum species are similar to **1** in that oxidative addition occurs by net R^+ coordination without the formation of metal halide products such as $CpFe(CO)_2X$ or $Re(O)I(RC{\equiv}CR)_2$ (**4**) (even though halide complexes are the dominant products in other radical oxidative addition processes[38]). This is because addition of R^+ leads to 18-electron compounds such as $CpFe(CO)_2R$ or $Re(O)R(R'C{\equiv}CR')_2$. In the rhenium case, the lack of formation of **4** is also due to the instability of $[Re(O)I(RC{\equiv}CR)_2]^{\bullet-}$ and to the rapid reaction of **4** and **1** to give dimers.[13b] $CpFe(CO)_2^-$ and $Mo(CO)_2(dmpe)_2$ are themselves 18-electron complexes, so addition of R^+ yields 18-electron species.[39] In compounds **1**, the HOMO (Figure 1) is Re–O π antibonding[40] so that the rhenium–oxygen bond is more like a double bond than a triple bond. Addition of R^+ to

(29) Further reduction of aryl radicals to aryl anions by **1** could also lead to the arene-d_1, by deprotonation of acetonitrile, but then it is not at all clear how the acetonitrile anion, CH_2CN^-, would combine with electron-rich **1** (or $Re(O)(RC{\equiv}CR)_2{}^{\bullet}$) to form **9**.

(30) Barrette, W. C., Jr.; Johnson, H. W., Jr.; Sawyer, D. T. *Anal. Chem.* **1984**, *56*, 1890–1898.

(31) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41–49. Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263. Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945–3953. Kristjánsdóttir, S. S.; Norton, J. R. *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH Publishers: New York, 1991 (in press).

(32) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; American Chemical Society: Washington, DC, 1983.

(33) For another example of the trapping of aryl radicals by solvent, see: Albertin, G.; Antoniutti, S.; Bordignon, E. *Organometallics* **1990**, *9*, 2177–2179.

(34) A radical chain process is also unlikely because of the instability of both $[Re(O)I(RC{\equiv}CR)_2]^{\bullet-}$ and $[Re(O)R'(RC{\equiv}CR)_2]^{\bullet-}$. [$Re(O)R(RC{\equiv}CR)_2$ shows no reduction wave in its cyclic voltammogram.]

(35) While halogen atom abstraction by **1** is unlikely, abstraction by the neutral rhenium radical, $Re(O)(RC{\equiv}CR)_2{}^{\bullet}$, can occur: this is the likely mechanism for the formation of $Re(O)X(RC{\equiv}CR)_2$ in reactions of **1** and CHX_3. Reactions of monohaloalkanes do not yield rhenium halides, which argues against this pathway (although it is possible that the $Re(O)X(RC{\equiv}CR)_2$ formed would be completely consumed by reaction with **1** to form dimers).

(36) Patai, S., Ed. *The Chemistry of the Carbon-Halogen Bond*; Wiley-Interscience: New York, 1973. See also ref 10a and references cited therein.

(37) Krusic, P. J.; Fagan, P. J.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 250–252. Connor, J. A.; Riley, P. I. *J. Chem. Soc., Chem. Commun.* **1976**, 634–635.

(38) Reference 10a, pp 306–319.

(39) Electron counting in compounds **1** is not simple due to the presence of both oxo π donation and Re–O π antibonding; this issue will be discussed in more detail in a future publication.

(40) The HOMO in **1** is also Re–acetylene back-bonding.

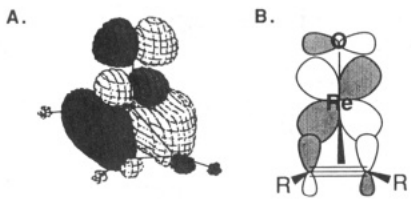


Figure 1. Drawings of the HOMO of $[Re(O)(RC{\equiv}CR)_2]^-$: (A) based on extended Hückel calculations;[45] (B) schematic picture showing the Re–O π-antibonding and Re–acetylene π-back-bonding interactions (for clarity, the second acetylene is not shown).

rhenium formally removes the electrons from this π^* orbital and thus allows increased π donation from the oxo ligand, giving the Re≡O bond found in the oxo–alkyl complexes. This improvement in Re–O bonding on addition of an acid or on loss of electrons may be a cause of the high reactivity of compounds **1**.

The mechanism of oxidative addition to **1** changes from nucleophilic displacement for MeI and acetic anhydride to electron transfer for tertiary alkyl halides and aryl halides. This is common for metal nucleophiles, from the $CpFe(CO)_2^-$ system mentioned above[37] to $PtMe_2(phen)$,[41] because of steric problems bringing together crowded metal and carbon centers (S_N2 reactions at tertiary carbons are very rare even with small organic nucleophiles). The reactions of primary and secondary alkyl halides with **1** may occur by a mixture of the two mechanisms: dimers are clearly formed by a radical path, but the oxo–alkyl complexes could be the result of either nucleophilic attack or radical combination. Similarly, the formation of the oxo–phenyl products **8** from **1** and PhX in benzene solution could occur by nucleophilic or radical paths. The reaction of 6-iodo-1-hexene and **1a** in dilute solution yields only 20% of the hexenyl complex **5**, so at most 20% of the reaction occurs by a nucleophilic mechanism.

The solvent dependence of many of the reactions (benzene vs acetonitrile) is likely due to the tight ion pairing of compounds **1** in solution. They are soluble even in pentane, existing as aggregates with sodium ions bridging between oxo groups (as found for **1c** in the solid state).[6] The importance of ion pairing is indicated by the effect of added 15-crown-5: The reaction of **1a** and PhI in the presence of 3 equiv of crown ether yields (in C_6D_6) less than 5% $Re(O)Ph(MeC{\equiv}CMe)_2$ (**8a**), versus 62% without crown, while in CD_3CN, the presence of crown prevents the formation of $Re(O)CD_2CN(MeC{\equiv}CMe)_2$ (**9a**) so that only dimers are observed. Crown influences the ratio of cyclized to uncyclized products in the 6-iodo-1-hexene reaction in C_6D_6 but has little effect in CD_3CN.[42] In light of these results, electron transfer from rhenium to the organic halide probably should not be described as a simple outer-sphere process. The halide likely acts as a ligand to the sodium cation in **1**, which facilitates electron transfer because the NaX salt can be formed directly.

The anions **1** are all strong bases and good reductants, but the diphenylacetylene derivative **1c** is significantly less reactive than the 2-butyne and 3-hexyne complexes **1a** and **1b**. **1a** and **1b** deprotonate acetone and react with aryl halides, while **1c** is inert to these reagents. The large difference is due to PhC≡CPh being a much better π acceptor than dialkylacetylenes. This has a pronounced effect on the chemistry of compounds **1** because their HOMO has rhenium–acetylene back-bonding character (Figure 1).[6]

The HOMO is also rhenium–oxygen π antibonding, as mentioned above, so that there is significant electron density on the oxo group (this is where the sodium ions bind in the structure of **1c**).[6] Electrophilic attack on **1** therefore can occur at oxygen, as observed in reactions with Me_3SiX reagents and with **4** (to give the asymmetric dimer in Scheme II).[13b] Initial attack of H^+ and Me^+ might also occur at oxygen, followed by subsequent rearrangement of the hydroxide or methoxide to give the observed hydride or methyl product (eq 10). Initial protonation at the oxo

$$\underset{\mathbf{1}}{NaRe(O)(RC{\equiv}CR)_2} + H^+ \rightarrow Na^+ + [Re(OH)(RC{\equiv}CR)_2] \rightarrow Re(O)H(RC{\equiv}CR)_2 \quad (10)$$

group seems particularly likely since protonation at oxygen is kinetically more facile than protonation at a metal center.[31] Rearrangements such as methoxide to oxo–methyl have been much discussed;[43] the clearest example is the rearrangement of tantalum alkoxides.[44] However, attempts to observe an intermediate hydroxide or methoxide species in this system (at low temperature and in the presence of acetylene as a trapping agent) have to date been unsuccessful. Even with hard Me^+ sources such as $Me_3O^+BF_4^-$, the methyl complex is the only observed product. Efforts are in progress to generate Re(I) hydroxide and methoxide species independently to test the possibility of this pathway.

Conclusion

The rhenium(I)–oxo anions **1**, $NaRe(O)(RC{\equiv}CR)_2$, are very strong bases and potent reducing agents. Both properties are unprecedented for a transition-metal terminal oxo complex. The high nucleophilicity of **1** is evident in its reactions with protic reagents (water, acetone) and methyl and acyl sources (e.g. MeI, acetic anhydride). Primary to tertiary alkyl halides and aryl halides react predominantly via a radical pathway, to give rhenium alkyl complexes and rhenium(II) dimers. These reactions appear to occur by initial electron transfer to the organic halide, consistent with the highly reducing nature of compounds **1**.

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(42) In C_6D_6, 6-iodo-1-hexene + **1a** gives 15% **2**, 41% **5**, 44% **6** without added crown, and 8% **2**, 55% **5**, 37% **6** with 3 equiv of 15-crown-5.

(43) Reference 5, pp 66, 246–248.

(44) van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347–5349. Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. *J. Mol. Catal.* **1987**, *41*, 21–39.

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