Synthesis and Reactivity of Rhenium(I) Tris(acetylene) Complexes ReX(RC≡CR)₃[1]

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Received October 18, 1988

Rhenium tris(acetylene) iodide complexes, ReI(RC≡CR)₃ (R = Me, **2a**; R = Et, **2b**), have been isolated as byproducts of the improved synthesis of Re(O)I(RC≡CR)₂ from Re(O)(I)₃(PPh₃)₂ and the alkyne. The tris(acetylene) complexes are spectroscopically similar to the tungsten compounds W(CO)(RC≡CR)₃, indicating that they adopt the same C_{3v} structure with parallel acetylene ligands. The rhenium compounds are thermally and air stable. Other derivatives of the rhenium tris(acetylene) unit are formed by replacement of the iodide ligand: AgSbF₆/pyridine forms the cationic complex [Re(RC≡CR)₃py]SbF₆ and methyllithium yields the fluxional methyl species Re(Me)(RC≡CR)₃.
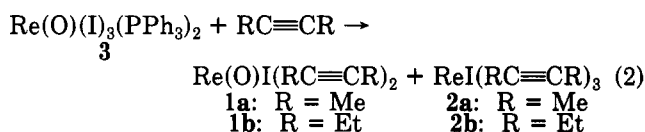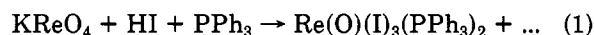
Acetylene ligands, because of their ability to act as both π donors and π acceptors, can stabilize metals in unusual coordination geometries and oxidation states. A classic example of an unusual acetylene complex is the series of tungsten tris(acetylene) carbonyl complexes, W(CO)(RC≡CR)₃.[4-7] These molecules have a C_{3v} structure resembling a tetrahedron or a capped trigonal prism, a very rare geometry for tungsten(0).[5] The tungsten attains an 18-electron configuration in these complexes through σ and π donation from the acetylene ligands, which, on average, act as $3^1/_3$-electron donors to tungsten.[4,7,8]

We have been studying rhenium oxo bis(acetylene) complexes Re(O)X(RC≡CR)₂ that are unusual both for their tetrahedral or pentagonal-pyramid structure and for the presence of a terminal oxo ligand in a formally low-valent complex.[9] The acetylene ligands act as three-electron donors to rhenium in these compounds. We now report that the synthesis of our primary starting material, Re(O)I(RC≡CR)₂, also yields a small amount of the tris(acetylene) complex ReI(RC≡CR)₃. These rhenium tris(acetylene) species are isoelectronic and apparently isostructural with the tungsten analogues.

Results and Discussion

Rhenium acetylene complexes Re(O)I(RC≡CR)₂ (**1**) and ReI(RC≡CR)₃ (**2**) are prepared by addition of excess acetylene to the rhenium(V) oxo iodide complex Re(O)(I)₃(PPh₃)₂ (**3**).[10] The rhenium(V) iodide species is made following the procedure for the chloride and bromide derivatives, from potassium perrhenate, aqueous HI, and triphenylphosphine in acetic acid (eq 1 and 2).[11] The iodide complex **3** is not isolated in pure form probably because some of the iodide present in reaction 1 is oxidized, forming I₃⁻ ions, I₂PPh₃, and OPPh₃.

$$KReO_4 + HI + PPh_3 \rightarrow Re(O)(I)_3(PPh_3)_2 + \dots \quad (1)$$

$$\underset{\textbf{3}}{Re(O)(I)_3(PPh_3)_2} + RC\equiv CR \rightarrow$$

$$Re(O)I(RC\equiv CR)_2 + ReI(RC\equiv CR)_3 \quad (2)$$

1a: R = Me	**2a**: R = Me
1b: R = Et	**2b**: R = Et

The overall yield of **1**, based on perrhenate, is consistently 80–95%. The yield of **2** varies from 0 to as much as 15%, depending primarily on the nature of the rhenium(V) starting material: the highest yields are obtained with fresh samples of **3**. Complex **3** gradually turns brown in a vial on the bench top, without significant change in its IR spectrum, and reactions of the brown material yield only **1**. This may be a result of partial hydrolysis of **3**, since **2** is not formed if water is added to reaction 2. The addition of water actually accelerates reaction 2 and gives **1** in high yield and purity.

Workup of the reaction mixture requires separation of **1**, **2**, and byproducts PPh₃, I₂PPh₃, and Ph₃PO. Our original procedure for the preparation of **1**[9] used the triphenylarsine starting material Re(O)I₃(AsPh₃)₂ instead of **3** because addition of iodine cleanly converted AsPh₃ to I₂AsPh₃ which could be removed by filtration. The chromatographic separation on silica gel reported here (see Experimental Section) removes the need for adding I₂ and gives high yields of **1** for both the AsPh₃ and PPh₃ starting materials. Formation of the tris(acetylene) compounds **2** is observed only when PPh₃ is used. Complexes **1** and **2** have almost identical R_f values so for complete separation we have utilized fractional crystallization, or sublimation of **1** away from **2**, or conversion of **1** to its methyl derivative Re(O)Me(RC≡CR)₂,[12] which is easily separated from **2** chromatographically.

The composition of **2a** and **2b** is indicated by their mass spectra, which show parent ions and strong base peaks for M⁺ – RC≡CR, and by analytical data. NMR spectra indicate that the ends of the acetylene ligands are inequivalent. There are two sets of alkyl resonances, and small (1 Hz) coupling is observed between the two methyl groups of the 2-butyne ligands of **2a**. Similar coupling is observed for **1a**.[9] The methylene hydrogens of the ethyl

(1) Low-Valent Oxo Compounds. 8. For the previous paper in this series see ref 12.

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Table I. ^{13}C Chemical Shifts of Acetylene Carbons

compound	$\delta(^{13}C)$	solvent
Re(I)(MeC≡CMe)$_3$ (2a)	168.3, 157.1	C$_6$D$_6$
Re(I)(EtC≡CEt)$_3$ (2b)	171.8, 162.8	C$_6$D$_6$
[Re(MeC≡CMe)$_3$py]SbF$_6$ (4)	181.3, 158.7	CD$_2$Cl$_2$
ReMe(MeC≡CMe)$_3$ (5)	177.8, 163.7	˙C$_6$D$_6$
W(CO)(EtC≡CEt)$_3$	191.1, 171.8[a]	a
W(CO)(PhC≡CPh)$_3$	192.5, 174.4[b]	CD$_2$Cl$_2$
[W(SnPh$_3$)(PhC≡CPh)$_3$]NEt$_4$	197.3, 183.3[b,c]	(CD$_3$)$_2$CO[c]

[a] Reference 8. Solvent not reported. [b] Reference 6g. [c] At 213 K.

groups in **2b** are not diastereotopic, unlike those in **1b**. These data show that **2a** and **2b** have a C_{3v} geometry (A), like the isoelectronic tungsten compounds W(CO)(RC≡CR)$_3$.
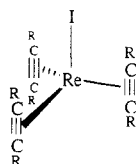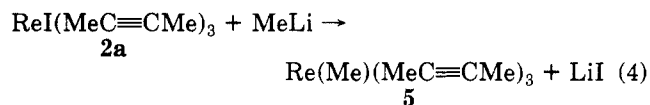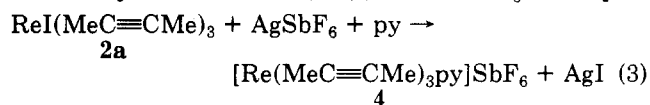

A

The spectra of the rhenium tris(acetylene) complexes **2** are quite similar to those of the tungsten analogues. In the proton NMR of the 3-hexyne compounds, for instance, $\delta(CH_2) = 3.45$ and 3.05 for **2b** and 3.54 and 3.07 for W-(CO)(EtC≡CEt)$_3$. In both the rhenium and tungsten compounds, rotation of the acetylene ligands does not occur on the NMR time scale. The lack of fluxionality of **2b** at 90 °C in C$_7$D$_8$ indicates that the barrier to acetylene rotation is greater than 18 kcal/mol. The IR spectra of both the Re and W compounds show a C≡C stretch in the region 1680–1760 cm^{-1} (R = Me, Et, Ph). The ^{13}C chemical shifts of the acetylenic carbons, which are a sensitive function of metal–acetylene bonding,[8] are in the range 157–181 ppm in the rhenium compounds and 171–197 ppm for the tungsten compounds (Table I). These chemical shifts are consistent with the acetylenes acting as $3^1/_3$-electron donor ligands, as suggested in the tungsten system on the basis of symmetry arguments and the 18-electron rule.[4,7,8]

Alternative synthetic routes to the tris(acetylene) compounds, either by oxygen abstraction from rhenium(III) oxo compounds or by treatment of Re(CO)$_5$I with 2-butyne, have not been successful. Re(O)I(MeC≡CMe)$_2$ (1a) does not react readily with PPh$_3$, and reactions with PMe$_3$ yield a mixture of products, one of which has been tentatively identified as [Re(PMe$_3$)$_3$(MeC≡CMe)$_2$]I.[9] Re-(O)Et(MeC≡CMe)$_2$ is unreactive with PMe$_3$ even at 80 °C.

The tris(acetylene) complexes are thermally stable: a benzene solution of **2a** shows no decomposition by NMR after 2 days at 100 °C in vacuo. **2a** does not react with 3-hexyne under these conditions, for instance, to exchange acetylene ligands.

The principal site of reactivity in the tris(acetylene) complexes is the iodide ligand. It can be removed with AgSbF$_6$, as illustrated by the preparation of pyridine adduct **4** (eq 3). Reaction of **2a** with methyl lithium yields the methyl derivative Re(Me)(MeC≡CMe)$_3$ (5) (eq 4).

$$\text{ReI(MeC≡CMe)}_3 + \text{AgSbF}_6 + \text{py} \rightarrow$$
2a
$$[\text{Re(MeC≡CMe)}_3\text{py}]\text{SbF}_6 + \text{AgI} \quad (3)$$
4

$$\text{ReI(MeC≡CMe)}_3 + \text{MeLi} \rightarrow$$
2a
$$\text{Re(Me)(MeC≡CMe)}_3 + \text{LiI} \quad (4)$$
5

Similar replacement of the iodide ligand has been observed in the oxo compounds **1** with AgSbF$_6$/pyridine and with dimethylzinc.[9,12] (Compounds **2a** and **2b** do not react with dimethylzinc.) For the W(CO)(RC≡CR)$_3$ compounds, there is only one report of an analogous ligand substitution reaction, replacement of the carbonyl ligand by PMe$_2$Ph.[6f] The tungsten species react with dmpe or ^{t}BuNC with loss of acetylene ligand(s),[6e] which is not observed for **2b** with excess PMe$_3$ over a month at 25 °C. Complex **4** does not react with DMSO or pyridine N-oxide.

The ^{1}H and ^{13}C NMR spectra of the pyridine complex **4** are similar to those of **2a**, with inequivalent acetylene methyl groups. Complex **5**, however, is fluxional on the NMR time scale. Two resonances are observed for the six acetylene methyl groups at −20 °C, but at 25 °C there is a single broad resonance. Resonances for free 2-butyne are sharp in the presence of **5**, and no exchange is observed on addition of excess 3-hexyne, indicating that 2-butyne rotation, not dissociation, is responsible for the coalescence. The barrier for rotation is roughly 15 kcal/mol.

The barrier to acetylene rotation is thus significantly lower for the methyl derivative than for the iodide or pyridine species. Fluxionality in the tungsten complexes W(L)(RC≡CR)$_3$ is dependent both on the nature of L and on the acetylene substituent. The carbonyl complexes are rigid on the NMR time scale for R = alkyl or aryl but fluxional for R = SiMe$_3$, SMe.[4,6] Replacing the CO ligand by the more electron-donating PMe$_2$Ph or R$_3$Sn$^-$ ligands lowers the barrier to rotation from 17.8 kcal/mol (W-(CO)(PhC≡CPh)$_3$, rigid at 25 °C) to 13.0 kcal/mol for the fluxional W(PMe$_2$Ph)(PhC≡CPh)$_3$ and [W(SnR$_3$)(PhC≡CPh)$_3$]$^-$ (R = Ph, Me).[6g,h] The origin of this trend seems to be electronic rather than steric, since the complex of the smallest ligand (methyl) is the most fluxional in the rhenium series while complexes of larger ligands are more fluxional for tungsten. Lower barriers to rotation are found with the more electron-donating ligands. This appears to be a transition-state effect because the metal–acetylene bonding is quite similar for these compounds in the ground state, on the basis of their ^{13}C NMR spectra (Table I).

Experimental Section

Reactions were performed on the bench without special precautions to avoid atmospheric oxygen or water, except as noted. NMR spectra were recorded on Varian CFT-20 and VXR-300 and Bruker CXP-200 and WM-500 spectrometers using C$_6$D$_6$ as solvent (unless otherwise stated). IR spectra were obtained as Nujol mulls (unless otherwise noted) using a Perkin-Elmer 283 spectrometer. Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS instrument using the direct inlet method with a 70 eV ionizing radiation (M$^+$ and base peak are reported). Elemental analyses were performed by Canadian Microanalytical Service Ltd., New Westminster, BC, Canada. 2-Butyne and 3-hexyne (Wiley Organics) were used as received; AgSbF$_6$ (Aldrich) was recrystallized from CH$_2$Cl$_2$/pentane and stored under nitrogen.

Re(O)I(MeC≡CMe)$_2$ (1a). ReO(I)$_3$(PPh$_3$)$_2$ (16 g, product from the synthesis below) and 2-butyne (8 g, 0.15 mol) were stirred in 150 mL of C$_6$H$_6$ for 48 h. The dark yellow solution was filtered through silica, concentrated, and loaded on a silica gel column. After the PPh$_3$ was washed off the column with hexanes, the yellow product was eluted with CH$_2$Cl$_2$ to afford, after solvent removal in vacuo, 4.55 g of **1a** as bright yellow crystals (88% based on KReO$_4$). Sublimation yields analytically pure material. If 1 mL of H$_2$O is added to the reaction flask at the start, the yields are slightly higher and the reaction is complete within 24 h. Spectroscopic and crystallographic data are reported in ref 9.

Re(O)I(EtC≡CEt)$_2$ (1b). ReO(I)$_3$(PPh$_3$)$_2$ (4 g) and 3-hexyne (2.8 g, 30 mmol) were stirred in 70 mL of C$_6$H$_6$ for 48 h. The dark solution was filtered, concentrated, and separated on silica gel as described for **1a** to afford 1.56 g of **1b** (93%) as a yellow oil. As for **1a**, addition of 1 mL of water causes the reaction to be

complete in 24 h. Spectroscopic data are reported in ref 9.

ReI(MeC≡CMe)₃ (2a). In oven-dried glassware, a suspension of 16.0 g (0.0144 mol) of 3 and 4.0 mL (0.051 mol) of MeC≡CMe in 100 mL of C₆H₆ was stirred for 3 days at 25 °C. After filtration, the solvent was removed using a rotary evaporator. The yellow-brown oil was chromatographed on silica gel using 1:9 ethyl acetate/hexanes (v/v), and a broad yellow band was collected. After solvent removal, crystallization of the yellow oil from pentane (5 mL) gave large colorless to pale green crystals, contaminated with yellow crystals of 1a, which were removed by hand. The yield of 2a was 0.82 g (15% based on KReO₄). The major product of this synthesis is 1a; yields of 2a are variable, and occasionally none is obtained, for as yet undetermined reasons. 1a could also be removed by sublimation at 75 °C or by conversion to Re-(O)Me(MeC≡CMe)₂ with excess ZnMe₂ and chromatography.[12] IR: 1753 w, 1354, 1169, 1068, 1046, 826 w, 796 w, 719 w, 638 cm⁻¹. ¹H NMR: δ 2.74 (q, 1 Hz), 2.47 (q, 1 Hz) CH_3C≡CCH'_3. ¹³C{¹H} NMR: δ 168.25, 157.08 MeC≡CMe; 18.90, 16.58 CH₃C≡CCCH₃. MS: 476, 422. Anal. Calcd for C₁₂H₁₈ReI: C, 30.32; H, 3.82. Found: C, 30.66; H, 3.79.

ReI(EtC≡CEt)₃ (2b). Following the procedure for 2a, 16.0 g (0.0144 mol) of 3 and 9.0 mL (0.080 mol) of EtC≡CEt in 100 mL of C₆H₆ gave 0.69 g of 2b (11% based on KReO₄). IR: 1738 w, 1724 w, 1413, 1305, 1254, 1151, 1099, 1064, 1050, 945, 810 w, 692 w cm⁻¹. ¹H NMR: δ 3.45 (q, 7 Hz), 3.05 (q, 7 Hz) MeCH_2C≡CCH'_2Me; 1.04 (t, 7 Hz), 0.96 (t, 7 Hz) CH_3CH₂C≡CCH₂CH'_3. ¹³C{¹H} NMR: δ 171.81, 162.79 EtC≡CEt; 27.80, 27.30 MeCH₂C≡CCCH₂Me; 14.76, 13.78 CH₃CH₂C≡CCH₂CH₃. MS: 560, 478. Anal. Calcd for C₁₈H₃₀ReI: C, 38.64; H, 5.40. Found: C, 38.38; H, 5.33.

Re(O)(I)₃(PPh₃)₂ (3)[10] was prepared following the procedure for the bromide derivative:[11] KReO₄ (8.0 g, 27.6 mmol) was dissolved in 24 mL of 57% aqueous HI (Aldrich), and a suspension of 34.3 g of PPh₃ (Pressure, 0.13 mol) in 500 mL of acetic acid was added. After the solution was stirred for 24 h, the yellow product was isolated by filtration and was washed with diethyl ether (4 × 100 mL) to afford 37 g of impure 3, identified by its IR spectrum.[10] This product is used without further purification.

[Re(MeC≡CMe)₃py]SbF₆ (4). A solution of AgSbF₆ (36 mg, 0.11 mmol) in dry CH₂Cl₂ (15 mL vacuum transferred from CaH₂) was added to a mixture of 2a (44 mg, 0.09 mmol) and pyridine (8.5 μL, 0.11 mmol) and the reaction mixture stirred for 3 days. Filtration, removal of the solvent to 1 mL, and addition of cold hexane (0 °C) yielded 59 mg of 4 as a pale yellow powder (96%). IR (neat): 1608 (py), 1225, 1175, 1075, 1050, 905, 765 s, 710 s cm⁻¹. ¹H NMR (CD₂Cl₂): δ 9.18, 8.32, 7.97 (all m) C₅H_5N, ortho, meta, para respectively; 3.15 (s), 2.26 (s) CH_3C≡CCH'_3. ¹³C NMR (CD₂Cl₂): δ 181.25 (s), 158.67 (s) MeC≡CMe; 155.09 (d, 175 Hz), 140.28 (d, 166 Hz), 128.00 (d, 176 Hz) C₅H_5N; 18.20 (q, 130 Hz), 10.98 (q, 130 Hz) CH_3C≡CCCH₃. Anal. Calcd for C₁₂H₁₈ReI: C, 30.78; H, 3.50. Found: C, 31.10; H, 3.47.

Re(Me)(MeC≡CMe)₃ (5). MeLi (0.1 mL of a 1.6 M solution in Et₂O, Aldrich, 160 mmol) was added to 46 mg of 2a (0.10 mmol) in 6 mL of C₆H₆ at −78 °C. The mixture was stirred at 25 °C for 2.5 h, and after TLC showed the presence of unreacted 2, another 0.2 mL of MeLi was added to the solution and stirring continued for a day. The solvent was removed in vacuo and the residue dissolved in CH₂Cl₂. This solution was filtered through silica gel and on evaporation of the volatiles yielded 21 mg (60%) of 5, an off-white solid, in almost analytically pure form. IR: 1730 w, 1265, 1165 s, 1050, 740, 633 cm⁻¹. ¹H NMR (−20 °C, CD₃CN): δ 3.04 (s), 2.30 (s) CH_3C≡CCH'_3; 2.20 (s) ReCH_3. ¹³C{¹H} NMR: δ 177.78, 163.66 MeC≡CMe; 18.91, 12.25 CH₃C≡CCCH₃; 2.52, ReCH_3. Anal. Calcd for C₁₃H₂₁Re: C, 42.95; H, 5.82. Found: C, 43.60; H, 5.86.

Reactions of Homo- and Heterobinuclear Cobalt Carbonyls with Metal Carbonyl Hydrides

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Received October 27, 1988

HMn(CO)₅, HMo(CO)₃Cp, and HFe(CO)₂Cp (Cp = cyclopentadienyl) were found to react with Co₂(CO)₈ forming HCo(CO)₄ and the corresponding mixed-metal carbonyl dimers. It was shown that HMo(CO)₃Cp transferred the hydrogen atom to Co₂(CO)₈ and CoMn(CO)₉ in reversible processes. The substituted hydride HMn(CO)₄P-n-Bu₃ and Co₂(CO)₈ afforded (CO)₄CoMn(CO)₄P-n-Bu₃ which was characterized by elementary analysis and IR and mass spectroscopy. Its reaction with HMo(CO)₃Cp gave HMn(CO)₄P-n-Bu₃ and CoMo(CO)₇Cp. The attack of the hydrides took place in mixed-metal complexes exclusively on the cobalt atom. A mechanism in which the hydrides oxidatively add to a coordinatively unsaturated Co center formed by CO loss is proposed.

Introduction

Hydrogen atom transfer from transition-metal carbonyl as well as HMR₃-type (M = Si, Ge, Sn; R = alkyl, aryl) metalloid hydrides to dinuclear carbonyl complexes became one of the most controversial reactions in metal carbonyl chemistry. A great number of reports appeared in recent years showing that such transformations could proceed either by UV irradiation[1] and room light[2] or under thermal conditions.[3-5] In many cases mechanistic investigations were also carried out. Although several different pathways were suggested, all agreed in assigning a role for metal carbonyl radicals as reactive intermediates. However, there are examples where the earlier mechanistic

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