870 *Organometallics* **2003,** *22,* 870−872

Notes

A Novel Example of the Reductive Cyclization of a Diyne at a Re−Re Triple Bond: The Reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ with 1,7-Octadiyne

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Received October 22, 2002

*Summary: The triply bonded dirhenium(II) complex $Re_2Cl_4(\mu\text{-dppm})_2$ (**1**; dppm = $Ph_2PCH_2PPh_2$) reacts with 1,7-octadiyne to produce the novel dirhenium(III) complex $Re_2Cl_3(\mu,\eta^2\text{-}C_8H_7)(\mu\text{-dppm})_2$ (**2**). The dirhenium complex **1** serves both as a reagent for the 2-electron reductive cyclization of the diyne and as the template to stabilize the resulting [$C_8H_7Re_2$] bridging unit, which is of a type not previously encountered in multiple bond dimetal chemistry.*

Introduction

The reversible redox behavior of complexes that contain the electron-rich triply bonded dirhenium(II) core has been well documented.[1] In addition, the ability of dirhenium(II) complexes to mediate the reductive coupling of organic molecules has been demonstrated in the reactions of the edge-sharing bioctahedral complexes $Re_2(\mu\text{-X})(\mu\text{-CO})X_3(L)(\mu\text{-dppm})_2$ (X = Cl when L = CO, XylNC; X = Br when L = CO; dppm = $Ph_2PCH_2PPh_2$) with terminal alkynes (including acetylene) in which the reductive coupling between the μ-CO ligand and the alkyne leads to carbon−oxygen bond formation and the generation of an unusual 3-metallafuran ring.[2]

We previously examined the reactions of acetylene with the redox active dirhenium(II) synthon $Re_2Cl_4(\mu\text{-dppm})_2$,[3−5] which contains an electron-rich $\sigma^2\pi^4\delta^2\delta^{*2}$ triple bond, with the expectation that reductive coupling would ensue. However, we observed[6] only η^2- and μ-η^2:η^2 coordination of acetylene to the dirhenium(II) unit with up to three acetylene molecules being incorporated into the coordination sphere (Scheme 1). We have now turned our attention to a study of the reactions of $Re_2Cl_4(\mu\text{-dppm})_2$ with dialkyne ligands and in the case of 1,7-octadiyne we have obtained an unusual dirhenium complex in which the diyne has undergone a reductive cyclization with the concomitant oxidation of the dimetal core to dirhenium(III). This is the first example of its type in dirhenium multiple bond chemistry.

Experimental Section

Starting Materials. The compound $Re_2Cl_4(\mu\text{-dppm})_2$ (**1**) was prepared by the literature method,[5] while samples of 1,7-octadiyne were purchased from the Aldrich Chemical Co. Solvents were obtained from commercial sources and dried and distilled under a dinitrogen atmosphere before use. Reactions were caried out under an atmosphere of dinitrogen.

Synthesis of $Re_2Cl_3(\mu,\eta^2\text{-}C_8H_7)(\mu\text{-dppm})_2$ (2). A solution of **1** (0.25 g, 0.19 mmol) in toluene (25 mL) was treated with 2 equiv of 1,7-octadiyne (0.04 g, 0.39 mmol) and the resulting mixture refluxed for 4 h. The red mixture was then cooled to room temperature, the solvent evaporated under vacuum, and the residue extracted into 15 mL of THF. The extract was filtered and the filtrate layered with 5 mL of hexanes. The crop of red crystals (composition **2**·4THF) was filtered off and a suitable crystal selected for an X-ray structure determination. The remaining product was then dried under vacuum during which time most of the lattice THF was lost; yield 0.15 g (53%). Anal. Calcd for $C_{62}H_{59}Cl_3OP_4Re_2$ (i.e. **2**·THF): C, 52.34; H, 4.15. Found: C, 52.23; H, 4.46. This composition was supported by ^1H NMR spectroscopy (recorded in $CDCl_3$).

IR spectrum (KBr pellet, 1600−400 cm^{-1}): 1587 (w), 1573 (m−w), 1485 (m), 1432 (vs), 1362 (m), 1334 (w), 1310 (w), 1277 (w), 1191 (m−w), 1159 (w), 1132 (w), 1095 (s), 1062 (m−s), 1028 (m−w), 999 (m−w), 968 (vw), 901 (m−w), 846 (vw), 789 (s), 737 (vs), 691 (vs), 616 (w), 519 (vs), 507 (s), 479 (s), 426 (m). ^1H NMR ($CDCl_3$, δ): 13.86 (m, 1H, C_8H_7), 8.4 to 7.0 (m, 40H, C_6H_5), 4.94 (m, 2H, $-CH_2-$ of dppm), 4.80 (m, 3H, $-CH_2-$ of dppm (2H) overlapping C_8H_7 (1H)), ~3.8 (m, 8H, $-CH_2-$ of THF (4H) overlapping C_8H_7(4H)), 2.38 (m, 2H, C_8H_7), 1.90 (m, 4H, $-CH_2-$ of THF). $^{31}P\{^1H\}$NMR ($CDCl_3$, δ): −12.6, +0.7 (centers of the multiplets of an AA′BB′ pattern). Cyclic voltammogram (0.1 M $n\text{-}Bu_4NPF_6-CH_2Cl_2$, Pt-bead electrode, ν = 200 mV s^{-1}): $E_{1/2} = +0.58$ V (ΔE_p = 80 mV) and $E_{p,a} = 1.42$ V vs Ag/AgCl.

X-ray Crystallography. A single crystal of composition **2**·4THF was obtained by crystallization of the reaction product **2** from a THF/hexanes mixture. The data collection for **2**·4THF was carried out at 150(±1) K with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were

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10.1021/om0208772 CCC: $25.00
Publication on Web 01/15/2003

Scheme 1. Products from the Reactions of $Re_2Cl_4(\mu\text{-dppm})_2$ (1) with Acetylene (ref 6)

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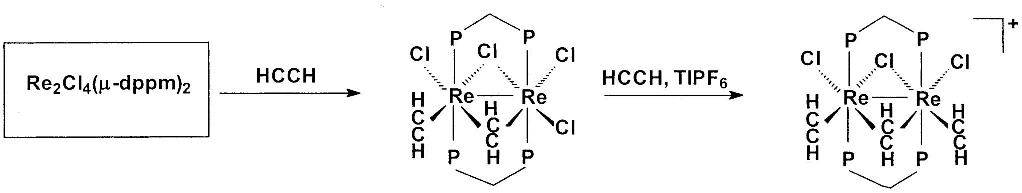

Table 1. Crystallographic Data for the Dirhenium Complex of Composition $Re_2Cl_3(\mu,\eta^2\text{-}C_8H_7)(\mu\text{-dppm})_2\cdot4THF$ (2·4THF)

empirical formula	$C_{74}H_{83}Cl_3O_4P_4Re_2$
fw	1639.14
space group	$P2_12_12_1$ (no. 19)
a, Å	13.9482(2)
b, Å	18.6857(2)
c, Å	26.2395(4)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	6838.9(3)
Z	4
ρ_{calcd}, g/cm^3	1.592
μ, mm^{-1}	3.843
radiation (λ, Å)	Mo Kα (0.71073)
temp, K	150
$R(F_o)^a$	0.042
$R_w(F_o^2)^b$	0.087
GOF	1.017

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

applied to the data sets. The key crystallographic data for **2**·4THF are given in Table 1. The structure was solved with the use of the structure solution program PATTY in DIRDIF92.[7] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with C−H = 0.95 Å and $U(H) = 1.3U_{eq}(C)$. They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK[8] was applied. The final refinements were performed by the use of the program SHELXL-97.[9] All non-hydrogen atoms were refined with anisotropic thermal parameters. The absolute structure was determined by refinement; the enantiomer chosen had an absolute structure parameter of 0.015(6).[10] The largest peak/hole in the final difference Fourier had a height of 1.09/−1.49 e/Å^3. The crystallographic drawing was done with use of the program ORTEP.[11]

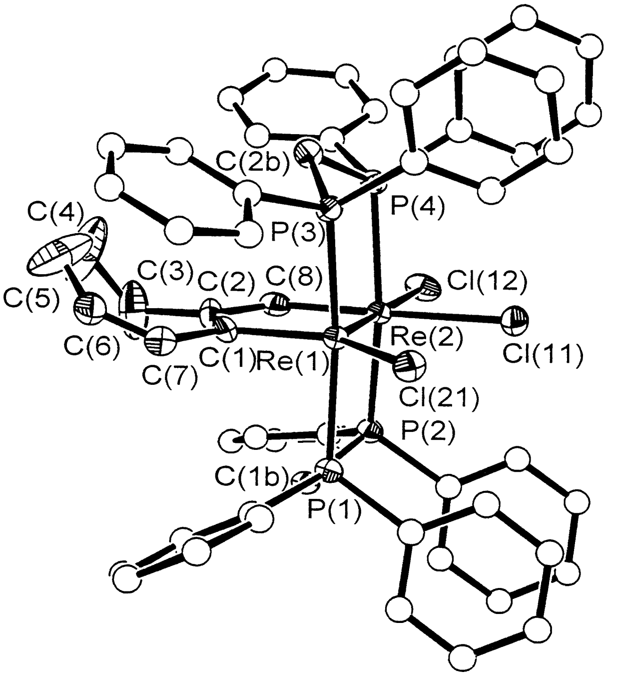

Figure 1. ORTEP[11] representation of the structure of the dirhenium complex $Re_2Cl_3(\mu,\eta^2\text{-}C_8H_7)(\mu\text{-dppm})_2$ as present in crystals of **2**·4THF. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl group carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Re(2) 2.2647(3), Re(1)−C(1) 2.019(6), Re(1)−Cl(21) 2.4370(16), Re(1)−P(1) 2.4308(17), Re(1)−P(3) 2.4380(17), Re(2)−C(8) 2.012(7), Re(2)−Cl(11) 2.5097(15), Re(2)−Cl(12) 2.5464(16), Re(2)−P(2) 2.4640(16), Re(2)−P(4) 2.4618(17), C(1)−C(2) 1.400(10), C(1)−C(7) 1.477(10), C(2)−C(8) 1.410(9), C(2)−C(3) 1.510(10), C(3)−C(4) 1.498(16), C(4)−C(5) 1.383(17), C(5)−C(6) 1.488(13), C(6)−C(7) 1.342(10); Re(1)−Re(2)−Cl(12) 179.45(5), C(1)−Re(1)−Cl(21) 138.3(2), C(8)−Re(2)−Cl(11) 176.8(2), Re(1)−C(1)−C(2) 120.8(5), C(1)−C(2)−C(8) 114.0(6), C(2)−C(8)−Re(2) 122.6(5), Re(1)−C(1)−C(7) 117.9(5), C(1)−C(2)−C(3) 122.7(6), C(8)−C(2)−C(3) 123.3(7), C(4)−C(3)−C(2) 114.5(9), C(5)−C(4)−C(3) 117.0(9), C(4)−C(5)−C(6) 124.9(10), C(7)−C(6)−C(5) 129.6(10), C(6)−C(7)−C(1) 126.8(7).

Physical Measurements. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 2000 FT-IR spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained with the use of a Varian INOVA 300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuterated solvent. The $^{31}P\{^1H\}$ spectrum was recorded at 121.6 MHz, with 85% H_3PO_4 as an external standard. Electrochemical measurements were carried out with use of a BAS Inc. Model CV-27 instrument in conjunction with a BAS Model RXY recorder and were recorded on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at 25 °C and were uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple.

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

The reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ with 1,7-octadiyne in refluxing toluene affords the red purple crystalline

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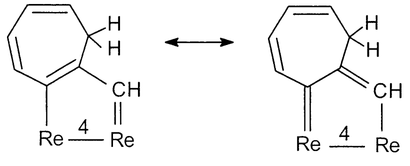
complex $Re_2Cl_3(\mu,\eta^2\text{-}C_8H_7)(\mu\text{-dppm})_2$ (**2**) (yield 50−60%), which is soluble in dichloromethane, chloroform, benzene, toluene, and tetrahydrofuran. Since the same product is formed when $TlPF_6$ is present, this reaction does not require the addition of a halide labilizing reagent. Crystals of **2** were obtained from THF/hexanes and were shown (by X-ray crystallography) to be of composition **2**·4THF. Partial loss of THF occurs under a vacuum to give **2**·THF as established by ^1H NMR spectroscopy and elemental microanalysis.

The ORTEP[11] representation of the dirhenium complex present in **2**·4THF is shown in Figure 1; the important bond distances and angles are given in the caption for this figure. There are four independent molecules of THF in the asymmetric unit. The structure determination establishes that a reductive cyclization of the 1,7-octadiyne has occurred and that the dirhenium unit retains a Re−Re multiple bond. The Re−Re distance of 2.2647(3) Å does not unequivocally distinguish between a Re−Re bond order of 4 or 3 especially in view of the presence of an axial Re−Cl bond at Re(2) that would lead to some weakening and lengthening of the Re−Re bond.[1] Indeed, dirhenium complexes that have the same bond order and similar structures can have significantly different Re−Re bond distances; for example, the distances are 2.234(3) and 2.2841(7) Å in $Re_2Cl_4(\mu\text{-dppm})_2$[4] and $Re_2(CH_3)_4(\mu\text{-dppm})_2$,[12] respectively. However, since **2** is diamagnetic it must be a derivative of the $[Re_2]^{6+}$ or $[Re_2]^{4+}$ core. The fact that the 1,7-octadiyne has undergone a reductive cyclization reaction supports **2** being a quadruply bonded dirhenium(III) complex. Its formation is in accord with the reaction stoichiometry shown in eq 1, although we have not been able to confirm that H_2 and HCl are formed

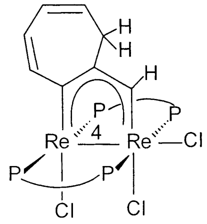
$$Re_2Cl_4(\mu\text{-dppm})_2 + C_8H_{10} \rightarrow Re_2Cl_3(\mu,\eta^2\text{-}C_8H_7)(\mu\text{-dppm})_2 + H_2 + HCl \quad (1)$$

under the reflux conditions we used for this reaction. Alkyne isomerization may be involved in the conversion of 1,7-octadiyne to this cyclized product, as is known to occur in mononuclear rhenium chemistry,[13] but the mechanism for this reaction is unknown.



A **B**

The nonplanar $\mu\text{-}C_8H_7$ ligand is formally trianionic and its bonding to the dirhenium core can be represented in terms of **A** and **B** being major contributing structures. This is supported by the similarity between the bridgehead C−C distances of 1.400(10) Å (for C(1)−C(2)) and 1.410(9) Å (for C(2)−C(8)) (see Figure 1). Furthermore, the Re−C distances of 2.019(6) Å (for Re(1)−C(1)) and 2.012(7) Å (for Re(2)−C(8)) are much shorter than the Re−C single bond distances of 2.15−2.17 Å in $Re_2(CH_3)_4(\mu\text{-dppm})_2$[12] and therefore consistent with some degree of multiple bonding as implied by the carbenoid character of the contributing structures **A** and **B**. On the basis of the foregoing discussion, a reasonable overall representation of the structure of **2** is that shown in **C**.



C

Within the seven-membered ring of **2**, the inequivalences in the C−C bond distances and the nonplanarity of the ring (see Figure 1) support the structural representation as shown in structure **C**. The C−C distances involving the methylene carbon C(3) are, as expected, consistent with single bonds (1.510(10) and 1.498(16) Å), while the bond distances within the five-carbon unit C(4)−C(5)−C(6)−C(7)−C(1) show alternating double bond−single bond character with the four distances being 1.383(17), 1.488(13), 1.342(10), and 1.477(10) Å, respectively.

The unsymmetrical nature of complex **2** is consistent with its $^{31}P\{^1H\}$ NMR spectrum, which shows multiplets of an AA′BB′ pattern centered at δ −12.6 and +0.7. Although the complex has an accessible and reversible one-electron oxidation at $E_{1/2} = +0.58$ V vs Ag/AgCl, we have not been able to isolate and characterize the oxidized cation $\mathbf{2}^+$.

The isolation of the dirhenium(III) complex **2** from the reaction of 1,7-octadiyne with **1** stands in marked contrast to the nonredox reactions of **1** with acetylene to give dirhenium(II) complexes that contain uncoupled η^2- and $\mu{:}\eta^2,\eta^2$-alkyne ligands.[6] In our attempts to extend this chemistry to other dialkynes we reacted **1** with 1,5-hexadiyne under a variety of reaction conditions but failed to isolate a pure crystalline and characterizable product. Further investigations of dialkynes await the completion of our studies on the reactions of **1** with monoalkynes other than ethyne.[6]

Acknowledgment. R.A.W. thanks the John A. Leighty Endowment Fund for support of this work.

Supporting Information Available: X-ray crystallographic data for **2**·4THF. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0208772

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