The Isolation and Characterization of a New Class of Mixed-valence Dirhenium Alkylidyne Complexes

Keng-Yu Shih, Phillip E. Fanwick and Richard A. Walton*

Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393 USA

The structural identity of the novel mixed-valence dirhenium alkylidyne complexes $[(L)ClRe(\mu\text{-}Cl)(\mu\text{-}CO)(\mu\text{-dppm})_2Re(\equiv CCH_2R)]Cl$ (dppm = $Ph_2PCH_2PPh_2$; L = CO or xylNC; R = Pr^n or Bu^n) formed *via* the ring-opening reactions of the 3-metallafuran complexes $[Re_2(\mu\text{-}Cl)\{\mu\text{-}COCH(R)CH\}Cl_2(L)(\mu\text{-dppm})_2]PF_6$, is established by an X-ray structure determination of the derivative where L = xylNC and R = Pr^n.

We have recently isolated the first examples of 3-metallafuran complexes through the reactions of terminal alkynes $RC\equiv CH$ (R = H, Pr^n, Bu^n, Ph or *p*-tol) with the edge-sharing bioctahedral complex $Re_2(\mu\text{-}Cl)(\mu\text{-}CO)Cl_3(L)(\mu\text{-dppm})_2$ (L = CO, xylNC; dppm = $Ph_2PCH_2PPh_2$).[1] These reactions (Scheme 1), which proceed in a stereospecific manner through C–O bond formation, form a metallacyclic ring for which canonical forms **A** and **B** make significant contributions.

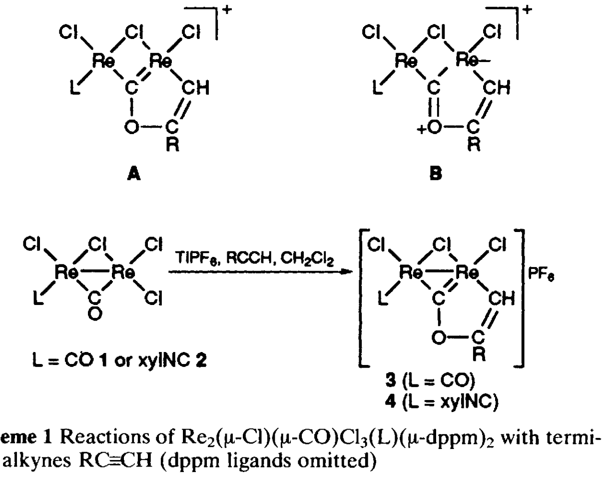
A consequence of the unsymmetrical nature of the 3-metallafuran ring in **3** and **4** is its susceptibility to ring opening when solutions of these complexes (R = Pr^n or Bu^n) are refluxed in polar solvents. These reactions afford green solutions which upon addition of diethyl ether yield the green, paramagnetic, alkylidyne complexes $[Re_2(\mu\text{-}Cl)(\equiv CCH_2R)Cl_2(CO)(L)(\mu\text{-dppm})_2]PF_6$ (L = CO for R = Pr^n **5a** or Bu^n **5b**; L = xylNC for R = Pr^n **6a** or Bu^n **6b**).† A one-electron reduction at $E_{1/2}$ *ca.* +0.29 V for **5** and *ca.* +0.03 V (*vs.* Ag/AgCl) for **6**, which is found in the cyclic voltammograms of solutions of **5** and **6** in 0.1 mol dm^{-3} $Bu_4{}^nNPF_6$–CH_2Cl_2, can be accessed chemically by the use of acetone solutions of $(\eta^5\text{-}C_5H_5)_2Co$ to afford the diamagnetic compounds $Re_2(\mu\text{-}Cl)(\equiv CCH_2R)Cl_2(CO)(L)(\mu\text{-dppm})_2$ (L = CO for R = Pr^n **7a** and Bu^n **7b**; L = xylNC for R = Pr^n **8a** or Bu^n **8b**). These complexes, like their oxidized congeners, possess a terminal ν(CN) or ν(CO) mode, and a semi-bridging ν(CO) mode in their IR spectra, at frequencies lower than those of the oxidized species;‡ this accords with an increase in Re → π*(CNR) and Re → π*(CO) back-bonding in the reduced compounds. These complexes display normal ^1H NMR spectra (CD_2Cl_2) for the bridging dppm ligands and the xylNC ligands, while the alkyl chains of the alkylidyne ligands display multiplets within the narrow chemical shift range δ −0.05 to +0.90. The $^{31}P\{^1H\}$ NMR spectra have the appearance of AA′BB′ patterns (*e.g.* for **7a** multiplets at δ −6.8 and δ −12.7).

The structure of a representative complex **8a** (crystals grown from CH_2Cl_2–*n*-heptane), which is shown in Fig. 1,§ not only confirms the presence of an alkylidyne unit [the $Re\equiv C$ distance of 1.70(1) Å is very short],[2,3] but reveals a very unsymmetrical edge-sharing bioctahedral structure with quite disparate Re–C distances for the semi-bridging CO ligand [1.87(1) and 2.62(1) Å]. The Re–Re distance [3.039(1) Å] signifies a weak Re–Re interaction. A marked charge disparity clearly exists in these complexes, which can be represented formally as mixed-valence Re^{II}–Re^{IV} species; the two 17-electron moieties can be considered to couple through a weak Re(μ-CO)Re bridging unit with the Re(1) centre being the more nucleophilic of the two.

While mononuclear rhenium alkylidyne complexes can be generated from the reactions of the rhenium polyhydride complex $ReH_4(mq)(PPh_3)_2$ with alkynes (mq is the monoanion of 2-mercaptoquinoline),[3] the decoupling reaction of the 2-metallated-3-metallafuran unit $\overline{Re(\mu\text{-}COC(R)CH)Re}$ of **3** and **4** provides a novel entry into metal alkylidyne chemistry. In the present case, it affords an unusual type of mixed-valence dirhenium complex. While the detailed mechanism is yet to be elucidated, the decoupling of the 3-metallafuran ring involves the net addition of a single hydrogen atom and is accompanied by a formal redox change from a $Re_2(8+)$ core in **3** and **4** to a $Re_2(7+)$ core in **5** and **6**. The source of the hydrogen can be the solvent, as shown by the reaction of **4** with hex-1-yne in CD_3OD or CH_3OD which leads to the incorporation of deuterium to give $[Re_2(\mu\text{-}Cl)(\equiv CCHDBu^n)Cl_2(CO)(CNxyl)(\mu\text{-dppm})_2]PF_6$ (^2H NMR spectrum in CH_2Cl_2, δ +0.45). Small amounts of water might be implicated as the source of hydrogen in the other solvent systems. The considerable stability of the $Re\equiv C$ unit is probably the driving force for the hydrogen transfer and concomitant ring opening to form **5** and **6**.

Support from the National Science Foundation (Grant CHE91-07578 to R. A. W.) is gratefully acknowledged.

Received, 2nd September 1993; Com. 3/05275C



Scheme 1 Reactions of $Re_2(\mu\text{-}Cl)(\mu\text{-}CO)Cl_3(L)(\mu\text{-dppm})_2$ with terminal alkynes $RC\equiv CH$ (dppm ligands omitted)

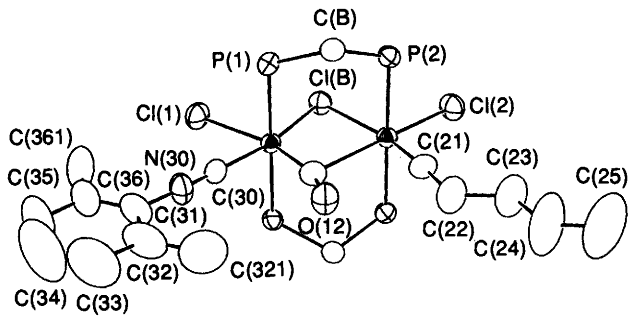


Fig. 1 ORTEP representation of the structure of the $Re_2(\mu\text{-}Cl)(\equiv CCH_2Pr^n)Cl_2(CO)(CNxyl)(\mu\text{-dppm})_2$ molecule in $\mathbf{8a{\cdot}2CH_2Cl_2}$ with the phenyl rings of the dppm ligands omitted. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and bond angles (°): Re(1)–Re(2) 3.0391(6), Re(1)–Cl(1) 2.475(3), Re(1)–Cl(B) 2.485(3), Re(1)–P(1), 2.409(2), Re(1)–C(11) 1.87(1), Re(1)–C(30) 1.95(1), Re(2)–Cl(2) 2.417(3), Re(2)–Cl(B) 2.542(3), Re(2)–P(2) 2.417(2), Re(2)–C(11) 2.62(1), Re(2)–C(21) 1.70(1), C(11)–O(12) 1.22(1), C(21)–C(22) 1.48(2), C(22)–C(23) 1.46(2); Re(1)–Cl(B)–Re(2) 74.39(7), Re(1)–C(11)–O(12) 158(1), Re(2)–C(21)–C(22) 174(1), C(21)–C(22)–C(23) 117(1).

Footnotes

† Isolated yields 30–50%. These complexes are ESR active (X-band spectra in CH_2Cl_2–toluene at −160 °C); for example, $g = 2.17$ (with Re hyperfine) for **6b**. Representative IR spectra (Nujol) are as follows: **5a** ν(CO) 2036(s) and 1816(m) cm^{-1}; **6a** ν(CN) 2152(s), ν(CO) 1802(m) cm^{-1}.

‡ For example: **7a** ν(CO) 1987(s) and 1804(m) cm^{-1}; **8a** ν(CN) 2078(s) and ν(CO) 1785(m) cm^{-1}.

§ *Crystal data* for **8a·2CH₂Cl₂** at +20 °C: space group *Pnma* with $a = 24.383(4)$, $b = 15.420(3)$, $c = 17.614(3)$ Å, $Z = 4$, $D_c = 1.650$ g cm^{-3}. An empirical absorption correction was applied. The final residuals were $R = 0.034$ ($R_w = 0.042$) and GOF = 1.228 for 3569 data with $I > 3.0\sigma(I)$. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 K.-Y. Shih, P. E. Fanwick and R. A. Walton, *J. Am. Chem. Soc.*, 1993, **115**, 9319.

2 For example, see: R. Toreki, R. R. Schrock and M. G. Vale, *J. Am. Chem. Soc.*, 1991, **113**, 3650.

3 M. Leeaphon, P. E. Fanwick and R. A. Walton, *J. Am. Chem. Soc.*, 1992, **114**, 1890.