Dinuclear Polyhydrides of Rhenium: Isolation and Characterization of Diamagnetic and Paramagnetic Complexes Containing the $[Re_2H_8]^{n+}$, $[Re_2H_7]^{(n+1)+}$, and $[Re_2H_5]^{(n+1)+}$ Cores (n = 0 or 1) Stabilized by Phosphine, Nitrile, and Isocyanide Ligands

Joe D. Allison and Richard A. Walton*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received May 19, 1983

Abstract: The electrochemical oxidation of the dirhenium octahydrides $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ (PR_3 = PPh_3, $PEtPh_2$, or PEt_2Ph) and $Re_2(\mu\text{-}H)_4H_4(AsPh_3)_4$ occurs at potentials between −0.15 and −0.40 V vs. SCE, to produce the corresponding paramagnetic, ESR-active monocations. This oxidation has been accomplished chemically in the case of the PPh_3 derivative using $Ph_3C^+PF_6^-$ and $C_7H_7^+PF_6^-$ as oxidants, dichloromethane as solvent, and a reaction temperature of 0 °C; the resulting product is $[Re_2\text{-}(\mu\text{-}H)_4H_4(PPh_3)_4]PF_6$. However, when the reaction with $Ph_3C^+PF_6^-$ is carried out in nitrile solvents, RCN (R = Me, Et, or Ph), then hydride abstraction occurs in preference to oxidation and the diamagnetic complexes $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCR)]PF_6$ are formed. The reaction of $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCMe)]PF_6$ with t-BuNC affords the substitution product $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(CN\text{-}t\text{-}Bu)]PF_6$. The complexes containing the $[Re_2H_7]^+$ moiety have been shown by cyclic voltammetric measurements (on 0.2 M Bu_4NPF_6–CH_2Cl_2 solutions) to exhibit two quasi-reversible one-electron oxidations (at ca. 0.0 and +0.70 V for the RCN derivatives and +0.19 and +0.94 V vs. SCE for the t-BuNC derivative). Oxidation to paramagnetic $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4L](PF_6)_2$ (for L = RCN or t-BuNC) has been achieved by using $NO^+PF_6^-$. In contrast to the sluggish reaction of $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ with t-BuNC, the oxidized monocation reacts extremely rapidly (in CH_2Cl_2 at 0 °C) to give $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$. Like the other polyhydrides this complex possesses two accessible one-electron oxidations, and it may be oxidized chemically to $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2](PF_6)_2$ very easily by using $NO^+PF_6^-$. While the diamagnetic complexes $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(CN\text{-}t\text{-}Bu)]PF_6$ and $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$ do not react significantly with excess t-BuNC within reasonable periods of time, their paramagnetic oxidized congeners do so extremely rapidly, the rhenium(I) complex $[Re(CN\text{-}t\text{-}Bu)_4(PPh_3)_2]PF_6$ and gaseous H_2 being the final products of these reactions. The complexes described in this report that contain the $[Re_2H_8]^+$, $[Re_2H_7]^{2+}$, and $[Re_2H_5]^{2+}$ cores constitute very rare examples of isolable radical cations of transition-metal hydrides, the first to be prepared for dimetal polyhydrides. The highly reactive nature of these species, compared to their far less reactive diamagnetic precursors, provides an important extension of the notion that paramagnetic electron-deficient organometallic species exhibit enhanced substitution lability relative to their 18-electron analogues.

Following the recognition that the "agnohydrides" or rhenium, $[ReH_x(PR_3)_2]_2$ (PR_3 = PPh_3 or a mixed alkyl–phenyl phosphine),[1] are in reality the dirhenium octahydrides $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$,[2] efforts have been under way to develop the chemistry of this novel series of complexes. In addition to studies directed toward the synthesis of[3] and an understanding of the bonding in[4] these molecules, their reactivity patterns are beginning to attract attention. Of special note are their reactions with organic chlorides[5] and phosphine ligands,[6] in which a dirhenium unit is preserved in the products. In the thermal reaction of $Re_2H_8(PMe_2Ph)_4$ with the phosphite ligand $P(OCH_2)_3CEt$ (abbreviated P′), loss of H_2

occurs to give the complex $Re_2(\mu\text{-}H)_3H(PMe_2Ph)_4P'_2$ possessing an unusual asymmetric structure.[6] Protonation of this molecule (using HBF_4) gives the symmetric conjugate acid $[Re_2(\mu\text{-}H)_3H_2(PMe_2Ph)_4P'_2]^+$.[6] This work, when taken in conjunction with the recent isolation of complexes of the type $Re_2(\mu\text{-}H)_3H_3(PR_3)_5$, via the photochemical reactions of mononuclear rhenium polyhydrides,[7,8] points to the existence of a variety of dirhenium polyhydride species.

In the present report we describe the isolation and characterization of a range of new complexes containing the $[Re_2H_8]^{n+}$, $[Re_2H_7]^{n+}$, and $[Re_2H_5]^{n+}$ cores, which in the case of $[Re_2H_8]^+$, $[Re_2H_7]^{2+}$, and $[Re_2H_5]^{2+}$ constitute *very rare examples of isolable radical cations of transition-metal hydrides, the first to be prepared for dimetal polyhydrides*.[9] The isolation of the diamagnetic complexes (derivatives containing the $[Re_2H_8]^0$,

(1) Chatt, J.; Coffey, R. A. *J. Chem. Soc. A* **1969**, 1963.

(2) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

(3) Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2674.

(4) Dedieu, A.; Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141.

(5) Allison, J. D.; Cameron, C. J.; Walton, R. A. *Inorg. Chem.* **1983**, *22*, 1599.

(6) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2319.

(7) Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1981**, *214*, 221.

(8) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695.

(9) Rhodes, L. F.; Zubkowski, J. D.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1982**, *21*, 4185 and references cited therein.

[Re₂H₇]⁺, and [Re₂H₅]⁺ moieties) and their paramagnetic congeners ([Re₂H₈]⁺, [Re₂H₇]²⁺, and [Re₂H₅]²⁺) permits us the opportunity to examine the effect of formally odd-electron metal centers on the reactivities of these metal polyhydride species. There is at present much interest in the enhanced subsitution lability of 17- and 19-electron organometallic species compared to their 18-electron analogues,[10] and our results now bring this topic into focus for a new group of complexes, namely, those containing dimetal polyhydride units.[11]

Experimental Section

Starting Materials. The following compounds were prepared by standard literature procedures: ReH₇(PR₃)₂ and Re₂(μ-H)₄H₄(PR₃)₄ (PR₃ = PPh₃, PEtPh₂, and PEt₂Ph),[1,12] ReOCl₃(AsPh₃)₂,[13] and *tert*-butyl isocyanide.[14] Ph₃C⁺PF₆⁻, C₇H₇⁺PF₆⁻, and NO⁺PF₆⁻ were purchased from Aldrich Chemical Co. and used as received. All solvents were purified by distillation from the appropriate drying agent.

Reaction Procedures. All reactions were carried out under an atmosphere of pure nitrogen and all solvents were deoxygenated prior to use by purging with nitrogen gas.

A. Preparation of Re₂(μ-H)₄H₄(AsPh₃)₄. A slurry of ReOCl₃(AsPh₃)₂ (1.0 g) in 30 mL of tetrahydrofuran was stirred at 0 °C while solid LiAlH₄ (0.3 g) was added over a period of 10 min. This mixture was allowed to react for a 3-h period, and the excess LiAlH₄ was then hydrolyzed by adding wet tetrahydrofuran dropwise at 0 °C until no further gas evolution was observed. The solvent was removed under vacuum and the brown residue was washed with ethanol and dried under vacuum. The remaining solid was extracted with carbon disulfide, and methanol was added to the filtrate to precipitate the red-brown complex; yield 0.20 g (12%). Anal. Calcd for C₇₂H₆₈As₄Re₂: C, 53.87; H, 4.27. Found: C, 53.15; H, 4.79.

B. Preparation of [Re₂(μ-H)₄H₄(PPh₃)₄]PF₆. A dichloromethane solution (5 mL) of Ph₃C⁺PF₆⁻ (0.041 g, 0.106 mmol) was added dropwise to a stirred solution of Re₂(μ-H)₄H₄(PPh₃)₄ (0.143 g, 0.100 mmol) in 10 mL of dichloromethane at 0 °C. The resulting blue solution was stirred for an additional 5 min, the solvent removed under vacuum, and the solid residue stirred under 15 mL of diethyl ether to afford a violet air-sensitive powder. This product was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.145 g (92%). Anal. Calcd for C₇₂H₆₈F₆P₅Re₂: C, 54.92; H, 4.35. Found: C, 55.02; H, 4.63.

Use of tropylium hexafluorophosphate, C₇H₇⁺PF₆⁻, in place of Ph₃C⁺PF₆⁻ produced this same complex in somewhat lower yield (62%).

C. Preparation of [Re₂(μ-H)₄H₃(PPh₃)₄(NCR)]PF₆ for R = Me, Et, and Ph. (i) **[Re₂(μ-H)₄H₃(PPh₃)₄(NCMe)]PF₆.** Trityl hexafluorophosphate (0.59 g, 0.152 mmol) in 10 mL of acetonitrile was added to a suspension of Re₂(μ-H)₄H₄(PPh₃)₄ (0.220 g, 0.154 mmol) in 15 mL of acetonitrile, and the mixture was stirred at room temperature. Within ca. 2 min, the Re₂(μ-H)₄H₄(PPh₃)₄ dissolved to yield a dark violet solution. The solvent was removed, diethyl ether was added, and the mixture was stirred for 30 min. The violet powder was filtered off, washed with diethyl ether, and recrystallized from dichloromethane/diethyl ether to give violet needles; yield 0.21 g (86%). Anal. Calcd for C₇₄H₇₀F₆NP₅Re₂: C, 55.05; H, 4.37. Found: C, 55.07; H, 4.58.

(ii) **[Re₂(μ-H)₄H₃(PPh₃)₄(NCEt)]PF₆.** A procedure similar to that in C(i) was used, substituting propionitrile for acetonitrile; yield 82%. Anal. Calcd for C₇₅H₇₂F₆NP₅Re₂: C, 55.31; H, 4.46. Found: C, 54.87; H, 4.76.

(iii) **[Re₂(μ-H)₄H₃(PPh₃)₄(NCPh)]PF₆.** This complex was prepared in a manner similar to that described in C(i), using benzonitrile; yield 84%. Anal. Calcd for C₇₉H₇₂F₆NP₅Re₂: C, 56.59; H, 4.33. Found: C, 57.42; H, 4.22.

D. Preparation of [Re₂(μ-H)₄H₃(PPh₃)₄(NCR)](PF₆)₂ for R = Me, Et, and Ph. (i) **[Re₂(μ-H)₄H₃(PPh₃)₄(NCMe)](PF₆)₂.** Solid NO⁺PF₆⁻ (0.03 g, 0.17 mmol) was added to a solution of [Re₂(μ-H)₄H₃(PPh₃)₄(NCMe)]PF₆ (0.150 g, 0.093 mmol) in 5 mL of acetone, whereupon the violet solution immediately turned blue. The solvent was stripped off and

the residue recrystallized from dichloromethane/diethyl ether to yield deep blue crystals; yield 0.145 g (89%). Anal. Calcd for C₇₄H₇₀F₁₂NP₆Re₂: C, 50.51; H, 4.01. Found: C, 49.77; H, 4.84.

(ii) **[Re₂(μ-H)₄H₃(PPh₃)₄(NCEt)](PF₆)₂.** Dark blue crystals of this complex were prepared by using a procedure analogous to D(i); yield 80%. Anal. Calcd for C₇₅H₇₂F₁₂NP₆Re₂: C, 50.79; H, 4.09. Found: C, 50.51; H, 4.11.

(iii) **[Re₂(μ-H₄)H₃(PPh₃)₄(NCPh)](PF₆)₂.** A procedure similar to D(i) was used; yield 93%. Anal. Calcd for C₇₉H₇₂F₁₂NP₆Re₂: C, 52.09; H, 3.98. Found: C, 52.49; H, 3.98.

E. Preparation of [Re₂(μ-H)₄H₃(PPh₃)₄(CN-t-Bu)]PF₆. A quantity of *tert*-butyl isocyanide (0.1 mL, 0.96 mmol) was syringed into a solution of [Re₂H₇(PPh₃)₄(NCCH₃)]PF₆ (0.105 g, 0.065 mmol) in 10 mL of dichloromethane and the reaction mixture stirred at room temperature for 1 h. The deep green solution was stripped to dryness, and the resulting green oil was stirred under diethyl ether for 1 h. The green powder was filtered off, washed with diethyl ether, and dried in vacuo. Recrystallization from dichloromethane/diethyl ether afforded the complex as green needles; yield 0.129 g (74%). Anal. Calcd for C₇₇H₇₆F₆NP₅Re₂: C, 55.82; H, 4.62. Found: C, 55.77; H, 5.03.

F. Preparation of [Re₂(μ-H)₄H₃(PPh₃)₄(CN-t-Bu)](PF₆)₂·CH₂Cl₂. This complex was isolated as small turquoise crystals from the reaction between NO⁺PF₆⁻ and [Re₂(μ-H)₄H₃(PPh₃)₄(CN-t-Bu)]PF₆ (0.102 g, 0.062 mmol) in acetone according to the procedure in D(i). Anal. Calcd for C₇₈H₇₈Cl₂F₁₂NP₆Re₂: C, 49.66; H, 4.17. Found: C, 49.25; H, 4.42. The presence of CH₂Cl₂ of solvation was confirmed by ¹H NMR spectroscopy (δ 5.35).

G. Preparation of [Re₂(μ-H)₃H₂(PPh₃)₄(CN-t-Bu)₂]PF₆. Details of the preparation of this complex through the reaction of [Re₂(μ-H)₄H₄(PPh₃)₄]PF₆ with *t*-BuNC in dichloromethane are described elsewhere.[15] An alternative procedure is as follows: *tert*-Butyl isocyanide (0.20 mL, 1.9 mmol) was added to a stirred solution of [Re₂(μ-H)₄H₃(PPh₃)₄(CN-t-Bu)](PF₆)₂ (0.15 g, 0.08 mmol) in 10 mL of dichloromethane whereupon the color of the solution changed from turquoise to yellow-green. After a reaction period of 2 h at room temperature, the solvent was evaporated under reduced pressure, and the residue was washed with diethyl ether and then dried in vacuo. Characterization of this material by cyclic voltammetry (in 0.2 M TBAH–dichloromethane) and ¹H NMR spectroscopy (in CD₂Cl₂) showed that it was a mixture (ca. 3:1) of [Re₂(μ-H)₃H₂(PPh₃)₄(CN-t-Bu)₂]PF₆ and [Re(CN-t-Bu)₄(PPh₃)₂]PF₆[12] (see also section I). No attempt was made to separate these products since more convenient methods exist for their preparation.

H. Preparation of [Re₂(μ-H)₃H₂(PPh₃)₄(CN-t-Bu)₂](PF₆)₂. Dark blue-turquoise crystals of this complex were prepared by the reaction of an acetone solution of NO⁺PF₆⁻ with [Re₂(μ-H)₃H₂(PPh₃)₄(CN-t-Bu)₂]PF₆ (0.055 g, 0.029 mmol) following a procedure similar to that described in D(i); yield 0.056 g (95%). Anal. Calcd for C₈₂H₈₃F₁₂N₂P₆Re₂: C, 52.31; H, 4.44. Found: C, 53.16; N, 4.91.

I. Reaction of [Re₂(μ-H)₃H₂(PPh₃)₄(CN-t-Bu)₂](PF₆)₂ with *tert*-Butyl Isocyanide. This reaction proceeded in a manner very similar to that described in section G between [Re₂(μ-H)₄H₃(PPh₃)₄(CN-t-Bu)]-(PF₆)₂ and *tert*-butyl isocyanide. However, in this instance, the ratio of the products [Re₂(μ-H)₃H₂(PPh₃)₄(CN-t-Bu)₂]PF₆ and [Re(CN-t-Bu)₄(PPh₃)₂]PF₆ was closer to 4:1. Once again product identification was based upon cyclic voltammetry and ¹H NMR spectroscopy.

J. Reaction of Re₂(μ-H)₄H₄(PPh₃)₄ with *tert*-Butyl Isocyanide. A quantity of Re₂(μ-H)₄H₄(PPh₃)₄ (0.20 g, 0.14 mmol) was refluxed in tetrahydrofuran (20 mL) with 0.2 mL (3.1 mmol) of *tert*-butyl isocyanide for a period of 4 days. The resulting red-brown solution was cooled to room temperature and the unreacted Re₂(μ-H)₄H₄(PPh₃)₄ (0.08 g) was filtered off. The filtrate was reduced to low volume and the resulting oil was dissolved in 15 mL of a saturated acetone/KPF₆ solution. The acetone solvent was removed under vacuum, and the insoluble product was washed with water and diethyl ether and then dried in vacuo. The product was identified as [Re(CN-t-Bu)₄(PPh₃)₂]PF₆ on the basis of its electrochemical and spectroscopic properties;[12] yield 0.07 g (20%).

Physical Measurements. Infrared spectral measurements of Nujol mulls were recorded in the region 4000–400 cm⁻¹ using KBr plates, with Beckman IR-12 and Acculab-6 spectrophotometers. ¹H NMR spectra (room temperature and variable temperature) were recorded at 90 MHz with a Perkin-Elmer R-32 spectrometer. Resonances were referenced internally to residual protons in the deuterated solvents. ³¹P NMR spectra were recorded on (CD₃)₂CO solutions using a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock using P(OMe)₃ as an external standard. X-Band ESR spectra were recorded at −160 °C on dichloromethane glasses of the complexes using a Varian E-109 spectrometer.

(10) See, for example: Shi, Q-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032.

(11) A recent attempt by Rhodes et al.⁹ to generate paramagnetic cations of the type [MoH₄(PR₃)₄]⁺ were unsuccessful. With use of AgBF₄ and HBF₄ in acetonitrile, the 18-electron species [MoH₂(PR₃)₄₋ₓ(NCMe)₂₊ₓ]²⁺ (x = 0 or 1) were generated.

(12) Allison, J. D.; Wild, R. E.; Wood, T. E.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 3540.

(13) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *Inorg. Synth.* **1967**, *9*, 145.

(14) Weber, W. D.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

(15) Allison, J. D.; Cotton, F. A.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1983**, *22*, 0000.

Dinuclear Polyhydrides of Rhenium

J. Am. Chem. Soc., Vol. 106, No. 1, 1984 165

Scheme I. Chemical Redox and Substitution Chemistry of Dirhenium Polyhydrides[a]

$Re_2H_8P_4 \xrightarrow{i} [Re_2H_7P_4(NCR)]^+ \underset{iv}{\overset{iii}{\rightleftharpoons}} [Re_2H_7P_4(NCR)]^{2+}$

$\downarrow v$

$[Re_2H_7P_4(CNR)]^+$

$iii \updownarrow iv$

$[Re_2H_7P_4(CNR)]^{2+} \xrightarrow{v} [Re(CNR)_4P_2]^+$

$[Re_2H_8P_4]^+ \xrightarrow{vi} [Re_2H_5P_4(CNR)_2]^+ \underset{iv}{\overset{iii}{\rightleftharpoons}} [Re_2H_5P_4(CNR)_2]^{2+}$

[a] P = PPh$_3$: (i) Ph$_3$C$^+$PF$_6^-$, RCN (R = Me, Et, Ph); (ii) Ph$_3$C$^+$PF$_6^-$, CH$_2$Cl$_2$, 0 °C; (iii) NO$^+$PF$_6^-$, acetone; (iv) Zn, CH$_2$Cl$_2$; (v) t-BuNC, CH$_2$Cl$_2$, room temperature; (vi) t-BuNC, CH$_2$Cl$_2$, 0 °C.
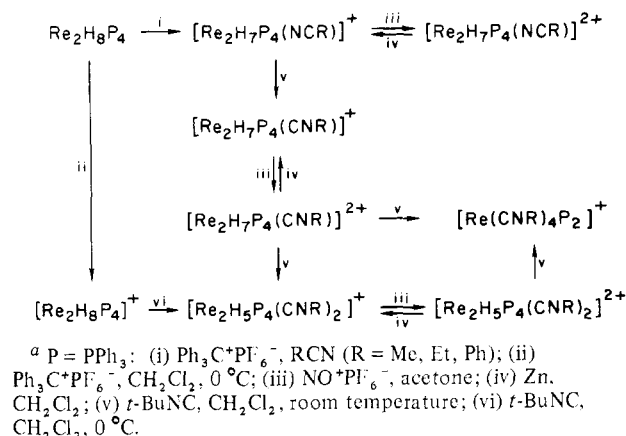
Cyclic voltammetry experiments were performed on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) were referenced to the saturated potassium chloride calomel electrode (SCE). Voltammetric measurements were taken with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. Conductivity data were obtained on $\sim 10^{-3}$ M acetonitrile solutions of complexes utilizing an Industrial Instruments Inc. Model RC-16B2 conductivity bridge.

Analysis of volatile gases were carried out using a Carle Series-S analytical gas chromatograph (Model 111-H 156A) equipped with a Linear Model 1201 strip-chart recorder. Reactions were sampled using the setup described previously.[5]

Microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

Redox Chemistry of Re$_2$(μ-H)$_4$H$_4$(PR$_3$)$_4$ (PR$_3$ = PPh$_3$, PEtPh$_2$, and PEt$_2$Ph) and Re$_2$(μ-H)$_4$H$_4$(AsPh$_3$)$_4$. In an earlier preliminary communication we reported[16] the electrochemical oxidation of Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$ to its dark blue paramagnetic monocation [Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$]$^+$, a species which we were able to characterize by ESR spectroscopy. Since this cation constituted a rare example of a paramagnetic transition-metal hydrido species, we decided to explore in more detail the redox chemistry of a selection of dirhenium octahydrides of this type. Furthermore, since we have succeeded in synthesizing for the first time an analogous arsine derivative, namely, Re$_2$(μ-H)$_4$H$_4$(AsPh$_3$)$_4$, these investigations have been extended to include this complex. The scope of this chemistry is shown in Scheme I, which summarizes the chemical redox and substitution reactions which have ensued from our studies of Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$.

The most general synthetic method for phosphine derivatives of the type Re$_2$(μ-H)$_4$H$_4$(PR$_3$)$_4$ is via the thermal decomposition of the mononuclear heptahydrides ReH$_7$(PR$_3$)$_2$,[1] complexes that are themselves prepared by the reaction of ReOCl$_3$(PR$_3$)$_2$ with LiAlH$_4$. During attempts to obtain the triphenylarsine complex Re$_2$(μ-H)$_4$H$_4$(AsPh$_3$)$_4$ by a similar method, we found that it can be prepared directly from the reaction of LiAlH$_4$ with ReOCl$_3$(AsPh$_3$)$_2$ at 0 °C in tetrahydrofuran. Apparently, under these mild reaction conditions, ReH$_7$(AsPh$_3$)$_2$ is much less thermally stable than ReH$_7$(PPh$_3$)$_2$ and loses hydrogen spontaneously to give the desired complex, albeit in low yield.[17] This complex, like its phosphine analogues, has moderate stability in the air and can be so handled for several hours without any noticeable sign of decomposition.

Table I. Electrochemical and X-Band ESR Spectral Data for Dirhenium Polyhydride Complexes

complex	$E_{1/2}(1)^a$	$E_{1/2}(2)^a$	g_{av}^b
Re$_2$H$_8$(PPh$_3$)$_4$	-0.20	+0.55^c	
Re$_2$H$_8$(PEtPh$_2$)$_4$	-0.26	+0.48^c	
Re$_2$H$_8$(PEt$_2$Ph)$_4$	-0.40	+0.38^c	
Re$_2$H$_8$(AsPh$_3$)$_4$	-0.16	+0.63^c	
[Re$_2$H$_8$(PPh$_3$)$_4$]PF$_6$	-0.20	+0.55^c	2.11
[Re$_2$H$_8$(PEtPh$_2$)$_4$]$^{+d}$	-0.25	+0.48^c	2.13
[Re$_2$H$_8$(PEt$_2$Ph)$_4$]$^{+d}$	-0.40	+0.39^c	2.11
[Re$_2$H$_8$(AsPh$_3$)$_4$]$^{+d}$	-0.16	+0.63^c	2.12
[Re$_2$H$_7$(PPh$_3$)$_4$(NCMe)]PF$_6$	+0.01	+0.73	
[Re$_2$H$_7$(PPh$_3$)$_4$(NCEt)]PF$_6$	-0.03	+0.72	
[Re$_2$H$_7$(PPh$_3$)$_4$(NCPh)]PF$_6$	+0.08	+0.70	
[Re$_2$H$_7$(PPh$_3$)$_4$(CN-t-Bu)]PF$_6$	+0.19	+0.94	
[Re$_2$H$_7$(PPh$_3$)$_4$(NCMe)](PF$_6$)$_2$	+0.01	+0.72	2.03
[Re$_2$H$_7$(PPh$_3$)$_4$(NCEt)](PF$_6$)$_2$	-0.03	+0.72	2.13
[Re$_2$H$_7$(PPh$_3$)$_4$(NCPh)](PF$_6$)$_2$	+0.08	+0.70	2.11
[Re$_2$H$_7$(PPh$_3$)$_4$(CN-t-Bu)](PF$_6$)$_2$	+0.19	+0.94	2.18
[Re$_2$H$_5$(PPh$_3$)$_4$(CN-t-Bu)$_2$]PF$_6$	+0.36	+1.13	
[Re$_2$H$_5$(PPh$_3$)$_4$(CN-t-Bu)$_2$](PF$_6$)$_2$	+0.36	+1.13	2.13

[a] Recorded at 0 °C on 0.2 M TBAH–CH$_2$Cl$_2$ solutions using a Pt bead electrode. In volts vs. SCE. [b] Recorded at -160 °C on CH$_2$Cl$_2$ glasses. [c] Irreversible couple; $E_{p,a}$ value given. [d] Electrochemically generated species.
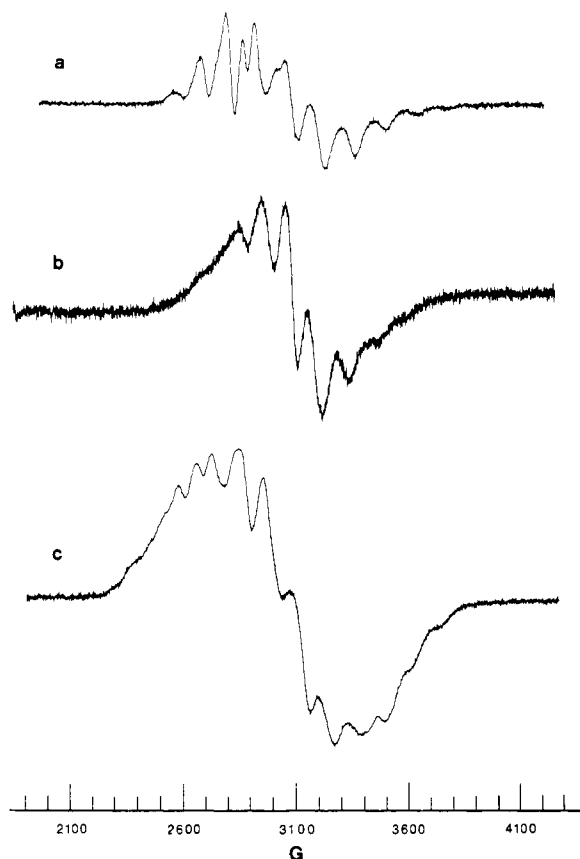
Each of the four dirhenium octahydrides exhibits very similar electrochemical behavior. The cyclic voltammograms (CV's) of 0.2 M TBAH–CH$_2$Cl$_2$ solutions of these complexes show a couple in the potential range -0.16 V to -0.40 V, corresponding to a one-electron oxidation, and an irreversible oxidation between +0.39 and +0.64 V vs. SCE (Table I). For the first oxidation, the peak current ratio $i_{p,a}/i_{p,c}$ equals unity and the values of $i_{p,c}/\nu^{1/2}$ were constant for scan rates (ν) from 50 to 400 mV/s. Values of $E_{p,a} - E_{p,c}$ (ca. 80 mV at 200 mV/s for all four complexes) increased with increasing scan rate. These properties are consistent with a quasi-reversible electron-transfer process. The $E_{1/2}$ and $E_{p,a}$ values (Table I) correlate with the basicity of the phosphine ($E_{1/2}$ for PPh$_3$ > PEtPh$_2$ > PEt$_2$Ph); i.e., oxidation is easiest with the most basic phosphine. In the case of Re$_2$(μ-H)$_4$H$_4$(AsPh$_3$)$_4$, its electrochemical properties correlate with AsPh$_3$, being, as expected,[18] a weaker base than PPh$_3$.

Bulk electrolyses at +0.20 V (n = 1.0 ± 0.1) were carried out at 0 °C to generate solutions containing the violet colored [Re$_2$(μ-H)$_4$H$_4$(PR$_3$)$_4$]$^+$ cations (blue in the case of PR$_3$ = PPh$_3$). Regeneration of the dark red solutions of the neutral diamagnetic precursors was achieved by reduction at -0.50 V.

The first oxidation can be achieved chemically by using a mild oxidant such as Ph$_3$C$^+$PF$_6^-$ or C$_7$H$_7^+$PF$_6^-$ (Scheme I). Addition of Ph$_3$C$^+$PF$_6^-$ to a dichloromethane solution of Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$ led to quantitative generation of [Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$]PF$_6$ in ca. 30 s. This isolable but rather air-sensitive salt exhibits the same electrochemical and spectral properties as do electrochemically generated solutions of [Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$]$^+$. The complex [Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$]PF$_6$ constitutes the first example of a crystalline paramagnetic polyhydride of rhenium. Our attempts to obtain other salts of this type were less successful, since while these same chemical oxidants gave rise to the appropriate color changes the resulting salts were very unstable and we were unable to isolate them in a sufficiently pure state. Accordingly, we focused our attention upon the triphenylphosphine derivative, which is, like its neutral analogue, the most stable of its congeners. In addition to its characteristic ESR spectrum (vide infra), its identity was confirmed by IR spectroscopy (ν(Re–H) at 1980 w and 1900 w cm^{-1}; ν(PF$_6^-$) at 840 vs cm^{-1}) and cyclic voltammetry ($E_{p,a}$ = +0.55 V and $E_{1/2}$(red) = -0.20 V vs. SCE).

X-band ESR spectral studies on CH$_2$Cl$_2$ glasses of the electrochemically generated dirhenium octahydride cations (at -160 °C), as well as on the salt [Re$_2$H$_8$(PPh$_3$)$_4$]PF$_6$, show that these species are characterized by a broad signal centered at g = 2.11–2.13 (Table I) which exhibits considerable hyperfine

(16) Allison, J. D.; Cameron, C. J.; Wild, R. E.; Walton, R. A. *J. Organomet. Chem.* **1981**, *218*, C62.

(17) This complex has the expected spectroscopic properties, with broad IR active ν(Re–H) modes at 1966 m, 1900 w and 1817 w cm^{-1} and an ^{1}H NMR spectrum (CS$_2$) with δ +7.25 (m, C$_6$H$_5$) and δ -6.66 (s, Re–H). The analogous phosphine derivatives Re$_2$(μ-H)$_4$H$_4$(PR$_3$)$_4$, which like the arsine complex are also fluxional, exhibit a pentet associated with Re–H at ca. δ -5.7(J(P–H) $\sim$ 9 Hz).[1–3,16]

(18) Mente, D. C.; Mills, J. L.; Mitchell, R. E. *Inorg. Chem.* **1975**, *14*, 123.

Figure 1. X-Band ESR spectra on CH_2Cl_2 glasses (-160 °C) containing (a) electrochemically generated $\{Re_2(\mu\text{-}H)_4H_4(PEtPh_2)_4\}^+$, (b) electrochemically generated $[Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4]^+$, and (c) $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCEt)](PF_6)_2$.

structure. While the ESR spectra of the PPh_3 and $PEtPh_2$ derivatives are very similar (that of $[Re_2(\mu\text{-}H)_4H_4(PEtPh_2)_4]^+$ is shown in Figure 1a),[19] they differ from those of the PEt_2Ph and $AsPh_3$ complexes in that the spectra of the latter are more symmetrical. The ESR spectrum of $[Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4]^+$ is presented in Figure 1b; that of $[Re_2(\mu\text{-}H)_4H_4(AsPh_3)_4]^+$ is less well resolved and accordingly will not be discussed further in any detail. These spectra are best explained in terms of the unpaired electron being associated with an orbital delocalized over both rhenium atoms, the hyperfine arising from coupling to two Re nuclei ($I = \frac{5}{2}$). The expected and distinctive 11-line spectra are seen in the case of the PPh_3 and $PEtPh_2$ complexes (Figure 1a), with regular spacings of 140–150 G being clearly discernible at the higher fields. However, we are unable at present to account for the asymmetry in the signals at lower fields, although we are able to rule out the presence of ESR-active impurities by remeasuring the spectra of solutions following the electrochemical reduction of $[Re_2(\mu\text{-}H)_4H_4(PEtPh_2)_4]^+$ back to the neutral precursor complex. In the case of $[Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4]^+$ (Figure 1b), while the spectrum is more isotropic it is also more poorly resolved;[20] nonetheless, the regular spacings of 120 G are most likely assignable to rhenium hyperfine. Indeed, the magnitude of A^{Re} ($\sim 140 \times 10^{-4}$ cm^{-1}) in the complexes studied here is similar to that reported previously for multiply bonded dirhenium complexes containing halide and phosphine ligands.[21] The general similarity of the ESR spectra of $[Re_2(\mu\text{-}H)_4H_4(PEt_2Ph)_4]^+$ and

$[Re_2(\mu\text{-}H)_4H_4(AsPh_3)_4]^+$ is good evidence that the principle origin of the hyperfine structure is through coupling to the rhenium nuclei. While simple electron counting procedures could lead one to picture complexes of the type $Re_2(\mu\text{-}H)_4H_4L_4$ as containing formal Re–Re triple bonds,[2,3] and the monocation $[Re_2(\mu\text{-}H)_4H_4L_4]^+$ a Re–Re bond order of 2.5, such an extreme interpretation involving these high metal–metal bond orders is not required by the ESR spectral results. The bonding in complexes that contain M–H–M bridges can certainly be more complicated than this.[4] Nonetheless, the notion of some degree of multiple metal–metal bonding is a reasonable possibility.

Isolation and Characterization of $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCR)]PF_6$ (R = Me, Et, or Ph). Whereas 1:1 stoichiometric proportions of $Ph_3C^+PF_6^-$ and $C_7H_7^+PF_6^-$ oxidize $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ to its monocation when these reactions are carried out in dichloromethane at 0 °C, a different reaction course ensues in nitrile solvents (Scheme I). In acetonitrile, propionitrile, and benzonitrile the diamagnetic, violet crystalline complexes $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCR)]PF_6$ are formed in high yield (80–90%), together with Ph_3CH. Abstraction of H^- (to form Ph_3CH) and coordination of RCN is the dominant pathway in these polar coordinating solvents. There is no evidence that these reactions proceed via the prior formation of $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]^+$ and its reaction with the trityl radical, since we find in separate experiments that this cation (as its PF_6^- salt) does not appear to react with 4-(triphenylmethyl)-1-(diphenylmethylidene)-2,5-cyclohexadiene (the dimer of the trityl radical)[22] in the presence of RCN to afford $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCR)]^+$.

The ^1H NMR spectra of these complexes are in accord with their stoichiometry, the peak integrations being consistent with a stoichiometric ratio of 4:1 for the PPh_3:RCN resonances (R = Me or Et).[23] Resonances due to the phenyl rings were observed between δ 7.25 and 7.15, while additional resonances at δ 1.25 (singlet) for R = Me, and δ 1.57 (quartet) and δ 0.20 (triplet) for R = Et, signal the presence of the nitrile ligands. At room temperature (22 °C) the ^1H NMR spectra of CD_2Cl_2 solutions of the acetonitrile and propionitrile complexes showed a broad, structured, but poorly resolved Re–H resonance centered at δ ca. -5.0. When these solutions were cooled to about -70 °C, this resonance changed very little and did not split into resolvable resonances attributable to terminal and bridging Re–H units. In this respect the ^1H NMR spectra of these complexes resemble the related spectra of $Re_2(\mu\text{-}H)_4H_4(PR_3)_4^{1-3,16}$ in which rapid terminal-bridge interchange occurs even down to low temperatures. In the case of the $^{31}P\{^1H\}$ NMR spectrum of the acetonitrile complex (recorded in acetone-d_6 at 22 °C), two equally intense phosphine signals were observed at δ 32.31 and 31.50. When not proton decoupled, these signals were broadened considerably but did not reveal a distinctive splitting pattern.

In the case of the benzonitrile complex, we did not observe a Re–H resonance for its solutions in CD_2Cl_2, the same being true for $(CD_3)_2CO$ solutions of $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCMe)]PF_6$. Even for CD_2Cl_2 solutions of the acetonitrile and propionitrile complexes, the integrated intensities of the signals at δ -5.0, compared to signals arising from the RCN and PPh_3 ligands, were always lower than expected. An explanation in terms of H/D exchange would appear to be ruled out by the following observations. (1) The ^1H NMR spectrum of $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCMe)]PF_6$ in CD_2Cl_2 was found to be unchanged over a period of 12 h, there being no loss of hydride signal and no concomitant growth in the resonance due to the residual solvent protons. (2)

(19) The X-band ESR spectrum of a CH_2Cl_2 glass (-160 °C) containing $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]^+$ is shown in Figure 2 of ref 16.

(20) Note that while this signal is quite poorly resolved, its width is comparable to that of the corresponding spectrum of $[Re_2(\mu\text{-}H)_4H_4(PEtPh_2)_4]^+$ shown in Figure 1a. Furthermore, in addition to the five clearly resolvable hyperfine components, we observe four additional components (~ 140 G spacing) as shoulders in the wings of the broad signal. The two outer (and weakest) components of the expected 11-line spectrum were not detected.

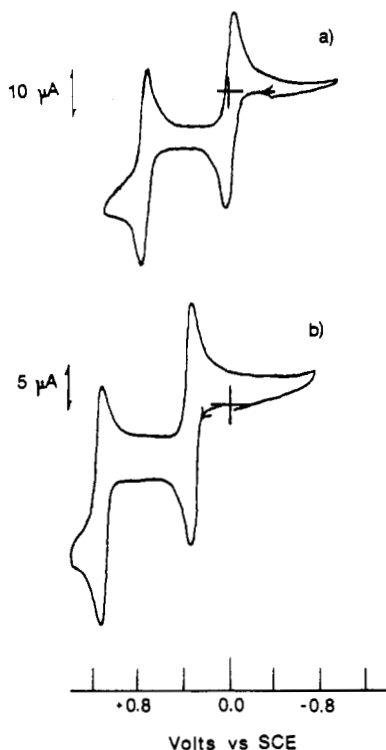(21) Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.

(22) (a) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009 and references therein. (b) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648.

(23) The Nujol mull IR spectra of these complexes proved to be less diagnostic of structure than we had hoped. In the region between 2400 and 1800 cm^{-1} where the $\nu(C\equiv N)$ and $\nu(Re-H)$ modes are expected, bands at 2270 m (R = Me), 2249 w (R = Et), and 2180 m cm^{-1} (with a shoulder at 2150 cm^{-1}) (R = Ph) showed the presence of coordinated RCN ligands. However, with the exception of a sharp band of medium–weak intensity in the IR of $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCMe)]PF_6$ that we assign to $\nu(Re-H)$, other $\nu(Re-H)$ absorptions in the IR spectra of RCN derivatives were very weak, broad, and poorly defined.

Figure 2. Cyclic voltammograms in 0.2 M TBAH–CH$_2$Cl$_2$ of (a) [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$(NCMe)]PF$_6$ and (b) [Re$_2$(μ-H)$_3$H$_2$(PPh$_3$)$_4$(CN-*t*-Bu)$_2$]PF$_6$; scan rate = 200 mV/s.

This same acetonitrile complex could be recovered unchanged (no D incorporation) when recrystallized from (CD$_3$)$_2$CO. Accordingly, these low hydride integrations are more than likely due to the relaxation problems that can affect transition-metal hydrides.[24] Note: while a structure for the nitrile complexes comprising four bridging Re–H–Re units and three terminal Re–H bonds is not proven by these spectral measurements, it remains, at this time, the most reasonable structural formulation.

All three complexes of the type [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$-(NCR)]PF$_6$ are soluble in acetonitrile to form solutions ($\sim 10^{-3}$ M) that possess conductivities (Λ_m = 100–132 Ω^{-1} cm^2 mol^{-1}) typical of 1:1 electrolytes.[25] Cyclic voltammetric measurements on 0.2 M TBAH–CH$_2$Cl$_2$ solutions of these complexes show that like the isoelectronic Re$_2$(μ-H)$_4$H$_4$(PR$_3$)$_4$ they possess two one-electron oxidations, but in these instances both couples meet the criteria for being quasi-reversible electron-transfer processes (Table I and Figure 2a). Controlled potential electrolysis at a potential of +0.20 V vs. SCE leads to a color change from violet to blue and the generation of quite stable solutions containing the paramagnetic radical cations [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$(NCR)]$^{2+}$. The first one-electron oxidation can be accomplished quite easily chemically upon the addition of NO$^+$PF$_6^-$ to acetone solutions of [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$(NCR)]PF$_6$ (Scheme I). When dichloromethane solutions of [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$(NCR)](PF$_6$)$_2$ were stirred with zinc metal, the monocationic species were regenerated. The structural formulation [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$-(NCR)](PF$_6$)$_2$ is supported by conductance measurements (Λ_m = 210–230 Ω^{-1} cm^2 mol^{-1} for 10^{-3} M solutions in acetonitrile) and the similarity of the ESR spectra (CH$_2$Cl$_2$ glasses at −160 °C) of these complexes to those of paramagnetic [Re$_2$(μ-H)$_4$H$_4$-(PR$_3$)$_4$]$^+$. The spectrum of [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$(NCEt)](PF$_6$)$_2$ is shown in Figure 1c, while the g_{av} values for the three paramagnetic nitrile derivatives are listed in Table I. A determination of the magnetic moment of [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$(NCMe)](PF$_6$)$_2$ was carried out by the Evans method (μ_{eff} = 1.4 ± 0.1 μ_B).

Reactions of [Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$]PF$_6$ and [Re$_2$(μ-H)$_4$H$_3$-(PPh$_3$)$_4$(NCMe)]PF$_6$ with *tert*-Butyl Isocyanide. We have found that the thermal reactions between Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$ and various nucleophiles can be extremely sluggish. Thus its reaction with *tert*-butyl isocyanide in refluxing tetrahydrofuran leads, after 4 days, to a low yield ($\sim 20\%$) of [Re(CN-*t*-Bu)$_4$(PPh$_3$)$_2$]PF$_6$ (identified on the basis of a comparison of its CV and spectroscopic properties to those of an authentic sample).[12] In contrast to this, the paramagnetic salt [Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$]PF$_6$ reacts rapidly (ca. 30 s) at 0 °C with isocyanide in dichloromethane to produce the diamagnetic salt [Re$_2$(μ-H)$_3$H$_2$(PPh$_3$)$_4$(CN-*t*-Bu)$_2$]PF$_6$ in high yield (Scheme I) with concomitant loss of H$_2$ (GC analysis). A 10^{-3} M solution of this complex in acetonitrile possessed a conductance (Λ_m = 103 Ω^{-1} cm^2 mol^{-1}) in keeping with its being a 1:1 electrolyte.[25] Full structural characterization of this molecule in the solid state and in solution is detailed elsewhere.[15] Suffice it to say that it bears a close structural relationship to the previously characterized salt [Re$_2$(μ-H)$_3$H$_2$(PMe$_2$Ph)$_4$[P-(OCH$_2$)$_3$CEt]$_2$]BF$_4$.[6] This reaction illustrates the tremendous enhancement in reaction rate associated with the *paramagnetic* dirhenium polyhydrides, further examples of which will follow.

In the case of the reaction of [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$-(NCMe)]PF$_6$ with *tert*-butyl isocyanide in dichloromethane, displacement of acetonitrile occurs to give [Re$_2$(μ-H)$_4$H$_3$-(PPh$_3$)$_4$(CN-*t*-Bu)]PF$_6$ (Scheme I), which is isolable in high yield after the reaction has proceeded for 1 h at 25 °C; further substitution does not occur, in accord with the correspondingly inert behavior of Re$_2$(μ-H)$_4$H$_4$(PPh$_3$)$_4$. Thus we encounter here an example of nonreductive substitution of a dirhenium polyhydride which can be mediated through the prior formation of an "activated" solvent complex (in this case acetonitrile).

The spectroscopic properties of [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$(CN-*t*-Bu)]PF$_6$ indicate that it possesses a structure analogous to that proposed for the related nitrile derivatives of this type. An IR-active ν(C≡N) mode at 2040 s cm^{-1} (with a shoulder at 2080 cm^{-1}) is in accord with the *t*-BuNC ligand being terminally bound; a band at 1976 m–w cm^{-1} may be assigned to ν(Re–H). The ^{1}H NMR spectrum (in (CD$_3$)$_2$CO) exhibits phenyl resonances at δ 7.30 (multiplet, broad) and a sharp singlet at δ 0.76 assignable to coordinated *t*-BuNC; these peaks integrate for a PPh$_3$:*t*-BuNC ratio of 4:1. In the hydride region, there is a broad resonance at δ −6.22 which is little changed over the temperature range +35 to −60 °C. While this signal has the correct integrated intensity when recorded for freshly prepared solutions, it diminishes in intensity when the solutions are allowed to stand and eventually disappears, even though the other proton resonances remain essentially unaffected. In this instance, the explanation seems to be that slow H/D exchange is occurring.

As we noted previously, the nitrile complexes [Re$_2$(μ-H)$_4$H$_3$-(PPh$_3$)$_4$(NCR)]PF$_6$ can be easily oxidized by NO$^+$PF$_6^-$ to the paramagnetic salts [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$(NCR)](PF$_6$)$_2$. Both [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$(CN-*t*-Bu)]PF$_6$ and [Re$_2$(μ-H)$_3$H$_2$-(PPh$_3$)$_4$(CN-*t*-Bu)$_2$]PF$_6$ not only exhibit rather similar electrochemical properties to the nitrile derivatives (see Table I and Figure 2b) but may be oxidized chemically by NO$^+$PF$_6^-$ in acetone solution (Scheme I) to the paramagnetic, ESR-active (see Table I) salts [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$(CN-*t*-Bu)](PF$_6$)$_2$ and [Re$_2$(μ-H)$_3$H$_2$(PPh$_3$)$_4$(CN-*t*-Bu)$_2$](PF$_6$)$_2$.[26] Both the latter salts display characteristic ν(C≡N) modes in their IR spectra (2116 ± 1 cm^{-1}) and are soluble in acetonitrile to give solutions with molar conductances typical of those expected for 1:2 electrolytes (Λ_m = 200–235 Ω^{-1} cm^2 mol^{-1} for 10^{-3} M solutions).[23] In comparing the CV data for the *tert*-butyl isocyanide and nitrile complexes of the type [Re$_2$(μ-H)$_4$H$_3$(PPh$_3$)$_4$L]$^{n+}$ (Table I and Figure 2), note the shift to more positive potentials of the couples for L = *t*-BuNC compared to L = RCN. This is explainable in terms of the greater π-accepting ability of *t*-BuNC compared to RCN, thereby leading

(24) Low integrated intensities for M–H resonances are quite frequently encountered. See: Jesson, J. P. "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Dekker: New York, 1971; p 75.

(25) Geary, W. J. *Coord. Chem. Revs.* **1971**, *7*, 81.

(26) The general features of the X-band ESR spectra of these salts (in CH$_2$Cl$_2$ at −160 °C) resemble those of the other paramagnetic dirhenium polyhydrido species displayed in Figure 1. Details of these spectra may be obtained from R.A.W.

to a greater withdrawal of electron density from the metal center, a subsequent lowering in energy of the HOMO, and thus an increase in the $E_{1/2}$ values; however, differences in σ-donor abilities are also a likely contributing factor.

Reactions of [Re₂(μ-H)₄H₃(PPh₃)₄(CN-*t*-Bu)](PF₆)₂ and [Re₂(μ-H)₃H₂(PPh₃)₄(CN-*t*-Bu)₂](PF₆)₂ with *tert*-Butyl Isocyanide. Whereas neither of the diamagnetic congeners of these two complexes reacts with excess *tert*-butyl isocyanide over reasonable periods of time, both the paramagnetic dications react quite rapidly (Scheme I). The dirhenium heptahydrido species reacts in dichloromethane to afford a 3:1 mixture of [Re₂(μ-H)₃H₂(PPh₃)₄(CN-*t*-Bu)₂]PF₆ and [Re(CN-*t*-Bu)₄(PPh₃)₂]PF₆ (as monitored by CV). In this reaction H₂ was identified by GC analysis as the only volatile gaseous product. When [Re₂(μ-H)₃H₂(PPh₃)₄(CN-*t*-Bu)₂](PF₆)₂ is reacted in this same fashion, the major product was the reduced monocation plus some [Re(CN-*t*-Bu)₄(PPh₃)₂]PF₆ (ca. 4:1 ratio of products).[27] Thus the formation of the diamagnetic monocationic dirhenium polyhydride species serves as a hindrance to the rapid and complete evolution of H₂ and the formation of the thermodynamic product [Re(CN-*t*-Bu)₄(PPh₃)₂]PF₆. This being the case, we reasoned that by keeping [Re₂(μ-H)₃H₂(PPh₃)₄(CN-*t*-Bu)₂]²⁺ in its oxidized state, i.e., preventing back reaction to the much more kinetically inert monocation, complete and rapid conversion to [Re(CN-*t*-

Bu)₄(PPh₃)₂]⁺ could be accomplished. This was proven by carrying out the reaction between [Re₂(μ-H)₃H₂(PPh₃)₄(CN-*t*-Bu)₂](PF₆)₂ and *tert*-butyl isocyanide in a CV cell at a potential of +0.50 V; this prevented reduction back to [Re₂(μ-H)₃H₂(PPh₃)₄(CN-*t*-Bu)₂]⁺ while at the same time ensuring that [Re(CN-*t*-Bu)₄(PPh₃)₂]⁺ was not oxidized ($E_{1/2}$ = +0.81 V vs. SCE).[12] By monitoring this reaction by CV we were able to show that rapid conversion to [Re(CN-*t*-Bu)₄(PPh₃)₂]⁺ occurred and that no significant quantities of [Re₂(μ-H)₃H₂(PPh₃)₄(CN-*t*-Bu)₂]ⁿ⁺ remained.

Registry No. Re₂H₈(PPh₃)₄, 66984-37-0; Re₂H₈(PEtPh₂)₄, 66984-38-1; Re₂H₈(PEt₂Ph)₄, 63313-85-9; Re₂H₈(AsPh₃)₄, 87901-15-3; [Re₂H₈(PPh₃)₄]PF₆, 86664-86-0; [Re₂H₈(PEtPh₂)₄]⁺, 87882-98-2; [Re₂H₈(PEt₂Ph)₄]⁺, 87882-99-3; [Re₂H₈(AsPh₃)₄]⁺, 87883-00-9; [Re₂H₇(PPh₃)₄(NCMe)]PF₆, 86664-85-9; [Re₂H₇(PPh₃)₄(NCEt)]PF₆, 87883-02-1; [Re₂H₇(PPh₃)₄(NCPh)]PF₆, 87883-04-3; [Re₂H₇(PPh₃)₄(CN-*t*-Bu)]PF₆, 86664-91-7; [Re₂H₇(PPh₃)₄(NCMe)](PF₆)₂, 86664-88-2; [Re₂H₇(PPh₃)₄(NCEt)](PF₆)₂, 87883-06-5; [Re₂H₇(PPh₃)₄(NCPh)](PF₆)₂, 87883-08-6; [Re₂H₇(PPh₃)₄(CN-*t*-Bu)](PF₆)₂, 86664-93-9; [Re₂H₅(PPh₃)₄(CN-*t*-Bu)₂]PF₆, 86676-29-1; [Re₂H₅(PPh₃)₄(CN-*t*-Bu)₂](PF₆)₂, 86676-31-5; [Re(CN-*t*-Bu)₄(PPh₃)₂]PF₆, 80006-29-7; ReOCl₃(AsPh₃)₂, 87863-04-5; Ph₃C⁺PF₆⁻, 437-17-2; C₇H₇⁺PF₆⁻, 29630-11-3; NO⁺PF₆⁻, 16921-91-8.

---

(27) The mechanism by which the reactive dicationic species [Re(μ-H)₃H₂(PPh₃)₄(CN-*t*-Bu)₂](PF₆)₂ is reduced back to its relatively unreactive monocationic congener is at present unknown.

Template Effects. 6.[1] The Effect of Alkali Metal Ions on the Formation of Benzo-3x-crown-x Ethers over a Wide Range of Ring Sizes

Luigi Mandolini* and Bernardo Masci*

Contribution from Centro C.N.R. di Studio sui Meccanismi di Reazione, c/o Istituto di Chimica Organica, Università "La Sapienza" di Roma, P.le Aldo Moro, 2 00185 Roma, Italy. Received April 12, 1983

Abstract: The rate of formation of benzo-3x-crown-x ethers with x = 4, 5, 7, 10, and 16 via intramolecular alkylation of *o*-⁻OC₆H₄(OCH₂CH₂)ₓ₋₁Br in 99% aqueous Me₂SO was found to be markedly affected by added alkali metal bromides. Catalysis or inhibition was observed, depending on the cation–substrate pair. Combination of the present results with those previously reported for the formation of B18C6 offers a large variety of patterns. The magnitude of the observed effects ranges over four powers of ten. The dependence of the observed rates (k_{obsd}) on metal ion concentration was expressed in terms of independent contributions from free and cation-paired aryl oxide ions, whose relative weights are ruled by the rate constants k_i and k_{ip}, respectively, and by the ion-pairing association constants K_{ArO^-}. A self-consistent analysis was used to derive numerical values of the above parameters. A definite contribution from an additional reaction path involving two metal ions was detected in the case of the K⁺-catalyzed formation of B30C10. The equilibrium constants K_C for associations between many cation–crown pairs were also determined under the same conditions. A comparative analysis of structure and metal ion effects on the extent of interaction of the alkali metal ions with the reactants, transition states, and reaction products shows that the cation interaction in the transition state is strongly reminiscent of the host–guest interactions found in the cation–B3xCx complexes. The catalytic efficiency of the alkali metal ions (log k_{ip}/k_i) shows a definite tendency to parallel the strength of interaction with the reaction products (log K_C), thus indicating that a metal ion capable of binding strongly with a crown ether is also a good catalyst for the formation of the crown ether itself.

In a recent paper[2] on the formation of benzo-18-crown-6 in 99% aqueous Me₂SO (eq 1, x = 6), we found that the catalytic effi-

ArO⁻   **B3xCx**   (1)
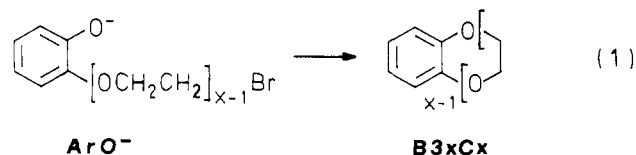
ciency of the alkali metal ions was closely related to the strength of interaction between the alkali metal ions and the reaction product, B18C6. Since associations between alkali metal ions and crown ethers are known to be highly dependent upon both the

(1) Part 5: Ercolani, G.; Mandolini, L.; Masci, B. *J. Am. Chem. Soc.*, **1983**, *105*, 6146.
(2) Illuminati, G.; Mandolini, L.; Masci, B. *J. Am. Chem. Soc.* **1983**, *105*, 555.