Negative solvatochromism has been well established for group 6 metal carbonyl species.[14-24] The energy (ν_{max} (10^3 cm^{-1})) of the MLCT transition of the mono- and bimetallic $[Re(CO)_3Cl]_{1,2}$dpp complexes was obtained from the absorption spectra of the complexes in several solvents (Table II) and plotted vs the E^*_{MLCT} parameter for the solvent in which the spectrum was acquired (Figure 2). The solvent sensitivity has previously been defined as $B = \nu_{max}/E^*_{MLCT}$.[19-21] The generally observed shift to higher energy of the MLCT transition in solvents of higher polarity has been attributed to ground-state stabilization of noncentrosymmetric complexes in more polar solvents.[17,21] Several centrosymmetric bimetallic complexes that have no permanent dipoles, such as $[(CO)_5W]_2$pz[19] and $[Mo(CO)_4]_2$bpm,[21] display larger B values than their monometallic analogues, and thus additional factors including molecular polarizability and σ-donating and π-back-bonding ability of the ligand have been utilized in the interpretation of the solvatochromic behavior. For the bimetallic $[Re(CO)_3Cl]_2$dpp complex, $B = 4007$ is larger than $B = 2678$ for the monometallic $[Re(CO)_3Cl]$dpp complex. Due to the fact that both the $[Re(CO)_3Cl]$dpp and $[Re(CO)_3Cl]_2$dpp complexes are noncentrosymmetric, and most likely contain permanent dipoles, the magnitude of B (increased solvatochromic sensitivity) of the bi- vs monometallic complexes can be attributed to a combination of increased molecular polarizability and dipole interactions. While exclusion of chlorinated solvents does not significantly alter solvatochromatic parameter values, THF causes an extreme deviation from linear behavior for the $[Re(CO)_3Cl]_2$dpp complex (Table II, Figure 2). The magnitude of B for the $[Re(CO)_3Cl]_{1,2}$dpp complexes is approximately equal to those reported for $[Mo(CO)_4]_{1,2}$bpm[21] (B = 3110, 4110) and $[Mo(CO)_4]_{1,2}$dpp[1b] complexes (B = 3060, 3257). Replacement of the CO group on a metal center by the electronegative Cl atom appears to have little effect on the B value, in comparison with previously noted replacements by electron-donating groups such as 2-pyridine or η^5-C_5R_5.[21] Solvatochromic values for $[Re(CO)_3Cl]_{1,2}$bpm and similar Re complexes were not reported.

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Strategy for the Synthesis of Mixed Phosphine–Phosphine, Phosphine–Arsine, and Phosphine–Stibine Complexes of the Types $Re_2H_8(PR_2Ph)_2(EPh_3)_2$ and $Re_2H_8(PRPh_2)_3(EPh_3)$ (R = Me, Et; E = P, As, Sb)

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The dirhenium octahydride complexes of stoichiometry $Re_2H_8(PR_3)_4$ constitute an important class of transition-metal polyhydride complexes whose structures,[1-4] redox characteristics,[5] and chemical reactivities[6-11] are of much current interest. Studies of their reactivity behavior have included protonation,[5,6] reactions with nucleophiles,[5,7,8] and reactions with copper(I),[9] gold(I),[10] and tin(II)[11] reagents. Many of these investigations have paralleled related studies on mononuclear rhenium polyhydrides, especially the very familiar heptahydrides $ReH_7(PR_3)_2$,[12] which also display a wide range of chemical reactivities[12-16] and interesting structural characteristics.[17] Of special note is the conversion of certain $ReH_7(PR_3)_2$ complexes to $Re_2H_8(PR_3)_4$ under thermal and photochemical conditions.[12,18]

While several different methods have been used in the past to generate the dirhenium octahydrides,[12,18-23] none were adapted to cover a wide range of phosphine ligands until we developed a synthetic strategy that we found was suitable for use with monodentate and bidentate phosphine ligands.[3,24] This utilized the dirhenium(II) complexes $Re_2Cl_4(PR_3)_4$[25-28] as starting materials and involved reaction with $LiAlH_4$ in glyme or THF. These one-pot reactions were dependent only upon the availability of the $Re_2Cl_4(PR_3)_4$ starting materials. In developing this procedure, we had reasoned that, with the use of starting materials that already contained the desired $(R_3P)_2ReRe(PR_3)_2$ architecture, i.e., $(PR_3)_2Cl_2ReReCl_2(PR_3)_2$, the strategy would be simplified and the yields optimized. This methodology requires that the phosphine ligands that are already bound to the dirhenium core not be labile, a condition that seems to be met. As a further development of this chemistry, we have examined how the dirhenium complexes $Re_2Cl_6(PR_3)_2$ and $Re_2Cl_5(PR_3)_3$,[25,29] which contain fewer than *four* phosphines, might be used to prepare mixed-phosphine complexes of stoichiometry $Re_2H_8(PR_3)_{4-n}(PR'_3)_n$ (n = 1 or 2), and closely related derivatives that contain

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phosphine–arsine and phosphine–stibine ligand sets. This has led to the isolation of the first examples of these types.[30] The details of our work are reported herein.

Experimental Section

Starting Materials. The complexes $Re_2Cl_6(PR_2Ph)_2$ (R = Me, Et)[25,31] and $Re_2Cl_5(PRPh_2)_3$ (R = Me, Et)[25] were prepared according to reported methods. The new complex $ReOCl_3(SbPh_3)_2$ was prepared by the following procedure. A solution of $SbPh_3$ (3.340 g, 9.5 mmol) in acetic acid (50 mL) was added to a slurry of $KReO_4$ (0.400 g, 1.4 mmol) and concentrated hydrochloric acid (5 mL). The resulting green suspension was stirred for 1 h, the mixture filtered, and the insoluble product washed with acetic acid (3 × 30 mL) and diethyl ether (3 × 30 mL) and dried under vacuum; yield 1.041 g (74%). Anal. Calcd for $C_{36}H_{30}Cl_3OReSb_2$: C, 42.61; H, 2.98. Found: C, 42.05; H, 2.99. The IR spectrum of this product (Nujol mull) showed a ν(Re=O) mode at 998 cm^{-1}.[32]

Samples of triphenylphosphine, triphenylarsine, and triphenylstibine were purchased from Pressure Chemical Co. and were used without further purification. Solvents used in the preparations of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed under an atmosphere of dry dinitrogen gas.

A. Synthesis of $Re_2H_8(EPh_3)_4$ (E = As, Sb). (i) $Re_2H_8(AsPh_3)_4$. A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.220 g, 0.20 mmol) and $AsPh_3$ (0.550 g, 1.8 mmol) was stirred with 15 mL of ethanol in an acetone/ice bath (−10 °C). After 30 min, an excess of $NaBH_4$ (0.140 g, 3.7 mmol) was added and the resulting suspension stirred for 20 h. The dark red precipitate was filtered off, washed with ethanol (15 mL) and methanol (3 × 15 mL), and dried under vacuum; yield 0.113 g (74%). Anal. Calcd for $C_{72}H_{68}As_4Re_2$: C, 53.86; H, 4.27. Found: C, 53.55; H, 4.64.

(ii) $Re_2H_8(SbPh_3)_4$. A quantity of $ReOCl_3(SbPh_3)_2$ (0.360 g, 0.36 mmol) was stirred in 15 mL of ethanol at −10 °C for 30 min. An excess of $NaBH_4$ (0.324 g, 8.8 mmol) was then added, the red suspension stirred for 20 h, and the mixture filtered, and the red solid was washed with ethanol (15 mL), methanol (3 × 15 mL), benzene (5 mL), and finally methanol (15 mL) once again. This product was then dried under vacuum; yield 0.082 g (26%). Anal. Calcd for $C_{72}H_{68}Re_2Sb_4$: C, 48.24; H, 3.82. Found: C, 48.36; H, 3.94.

B. Synthesis of $Re_2H_8(PMe_2Ph)_2(EPh_3)_2$ (E = P, As, Sb). (i) $Re_2H_8(PMe_2Ph)_2(PPh_3)_2$. A mixture of $Re_2Cl_6(PMe_2Ph)_2$ (0.115 g, 0.13 mmol) and PPh_3 (0.087 g, 0.33 mmol) was reacted with $NaBH_4$ (0.100 g, 2.6 mmol) in 15 mL of ethanol at −10 °C. The reaction procedure and workup was similar to that described in section A(i); yield 0.073 g (46%). Anal. Calcd for $C_{52}H_{64}O_2P_4Re_2$ (i.e., $Re_2H_8(PMe_2Ph)_2(PPh_3)_2\cdot 2H_2O$): C, 51.30; H, 5.30. Found: C, 51.78; H, 5.41.

Similar procedures were used to prepare the analogous arsine and stibine derivatives.

(ii) $Re_2H_8(PMe_2Ph)_2(AsPh_3)_2$. Yield: 60%.

(iii) $Re_2H_8(PMe_2Ph)_2(SbPh_3)_2$. Yield: 43%.

The triphenylarsine and triphenylstibine complexes were characterized on the basis of their electrochemical and spectroscopic properties.

C. Synthesis of $Re_2H_8(PEt_2Ph)_2(EPh_3)_2$ (E = P, As, Sb). (i) $Re_2H_8(PEt_2Ph)_2(SbPh_3)_2$. The reaction of $Re_2Cl_6(PEt_2Ph)_2$ (0.170 g, 0.19 mmol), $SbPh_3$ (0.151 g, 0.043 mmol), and $NaBH_4$ (0.203 g, 5.4 mmol) in 15 mL of ethanol at −10 °C was carried out with the use of a procedure and workup similar to that described in section A(i); yield 0.118 g (43%). Anal. Calcd for $C_{56}H_{72}O_2P_2Re_2Sb_2$ (i.e., $Re_2H_8(PEt_2Ph)_2(SbPh_3)_2\cdot 2H_2O$: C, 46.22; H, 4.99. Found: C, 46.51; H, 4.81.

The analogous PPh_3 and $AsPh_3$ complexes were obtained by use of a similar procedure; ^1H NMR spectroscopy showed them to be contaminated by very small amounts of other hydrido species.

(ii) $Re_2H_8(PEt_2Ph)_2(PPh_3)_2$. Yield: 56%.

(iii) $Re_2H_8(PEt_2Ph)_2(AsPh_3)_2$. Yield: 58%.

D. Synthesis of $Re_2H_8(PMePh_2)_3(EPh_3)$ (X = As, Sb). (i) $Re_2H_8(PMePh_2)_3(AsPh_3)$. A mixture of $Re_2Cl_5(PMePh_2)_3$ (0.198 g, 0.17 mmol) and $AsPh_3$ (0.061 g, 0.20 mmol) was stirred in 15 mL of ethanol for 30 min. An excess of $NaBH_4$ (0.200 g, 5.3 mmol) was then added and the mixture warmed to ca. 70 °C for 30 min. The reaction mixture was cooled to room temperature and filtered, and the insoluble dark red product was washed with ethanol (15 mL) and methanol (15 mL) and dried under vacuum; yield 0.154 g (69%). Anal. Calcd for $C_{57}H_{66}AsO_2P_3Re_2$ (i.e., $Re_2H_8(PMePh_2)_3(AsPh_3)\cdot 2H_2O$): C, 51.73; H, 5.03. Found: C, 51.67; H, 4.88.

(ii) $Re_2H_8(PMePh_2)_3(SbPh_3)$. The analogous $SbPh_3$ complex was prepared by use of a similar procedure, although ^1H NMR spectroscopy showed it to be contaminated by small amounts of other unidentified hydrido species; yield ca. 64%.

E. Synthesis of $Re_2H_8(PEtPh_2)_3(EPh_3)$ (E = As, Sb). (i) $Re_2H_8(PEtPh_2)_3(AsPh_3)$. The reaction between $Re_2Cl_5(PEtPh_2)_3$ (0.254 g, 0.21 mmol), $AsPh_3$ (0.075 g, 0.25 mmol), and $NaBH_4$ (0.256 g, 6.8 mmol) in 15 mL of ethanol was carried out at room temperature with the use of a procedure and workup similar to that in section D(i); yield 0.139 g (49%). Anal. Calcd for $C_{60}H_{72}AsO_2P_3Re_2$ (i.e., $Re_2H_8(PEtPh_2)_3(AsPh_3)\cdot 2H_2O$): C, 52.77; H, 5.31. Found: C, 52.85; H, 5.30.

(ii) $Re_2H_8(PEtPh_2)_3(SbPh_3)$. The analogous $SbPh_3$ derivative was prepared by the use of a similar procedure, but ^1H NMR spectroscopy showed it to be contaminated by a small amount of another hydrido species that was characterized by a peak at δ −6.44 (triplet), together with a trace amount of a material that also showed a triplet (δ −6.58); yield 25%.

Physical Measurements. IBM Instruments IR/32 and Perkin Elmer 1800 FTIR spectrometers were used to record infrared spectra of compounds as Nujol mulls supported on KBr plates in the region 4800–400 cm^{-1}. Electrochemical measurements were carried out by the use of a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A Pt-bead working electrode and a Pt-wire auxiliary electrode were utilized. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions, the ferrocenium/ferrocene couple is at $E_{1/2} = +0.47$ V vs Ag/AgCl. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated C_6D_6 solvent (δ +7.20). Phosphorus resonances were referenced externally to 85% H_3PO_4.

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

Results and Discussion

(a) Synthesis and Characterization of $Re_2H_8(AsPh_3)_4$ and $Re_2H_8(SbPh_3)_4$. As a prelude to attempting to synthesize mixed phosphine–phosphine, phosphine–arsine and phosphine–stibine complexes of dirhenium octahydride, we first examined synthetic routes to $Re_2H_8(AsPh_3)_4$ and $Re_2H_8(SbPh_3)_4$. The arsine complex had been reported previously, but it was prepared in very low yield (12%) from the reaction of $ReOCl_3(AsPh_3)_2$ with $LiAlH_4$ in THF at 0 °C, followed by hydrolysis of the reaction mixture.[5b] A preferable method is that in which a mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (1 equiv) and $AsPh_3$ (4 equiv) in ethanol is reacted with $NaBH_4$ at −10 °C (Scheme I). This procedure resembles one of the high-yield routes available to $Re_2H_8(PPh_3)_4$,[20,21] although in the latter case the reaction can be carried out at room temperature or above. Attempts by us to prepare $Re_2H_8(SbPh_3)_4$ by such a route did not afford a pure product. However, we did prepare this complex by the alternative method of reacting $ReOCl_3(SbPh_3)_2$ with $NaBH_4$ in ethanol at −10 °C. This is a variation of the procedure by which $Re_2H_8(PPh_3)_4$ and $Re_2H_8(AsPh_3)_4$ have been prepared from the reactions between $ReOCl_3(EPh_3)_2$ (E = P, As) and $LiAlH_4$ in THF and ethanol, respectively.[5b,12,21]

Scheme I. Routes to Dirhenium Octahydride Complexes from Dirhenium Starting Materials

$$(n\text{-}Bu_4N)_2Re_2Cl_8 + 4EPh_3 + NaBH_4 \xrightarrow{EtOH} Re_2H_8(EPh_3)_4 \qquad E = P, As \tag{1}$$

$$Re_2Cl_6(PR_2Ph)_2 + 2EPh_3 + NaBH_4 \xrightarrow[-10\ ^\circ C]{EtOH} Re_2H_8(PR_2Ph)_2(EPh_3)_2 \qquad R = Me, Et \quad E = P, As, Sb \tag{2}$$

$$Re_2Cl_5(PRPh_2)_3 + EPh_3 + NaBH_4 \xrightarrow{EtOH} Re_2H_8(PRPh_2)_3(EPh_3) \qquad R = Me, Et \quad E = As, Sb \tag{3}$$

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[30] We know of only one previous mention of a mixed-phosphine complex of a dirhenium polyhydride, namely, $Re_2H_6(PMe_2Ph)_4(PPh_3)$, although full details of its properties have not yet been reported; see: Sutherland, B. R.; Ho, D. M.; Huffman, J. C.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 135.

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[32] A related procedure, using concentrated aqueous HBr in place of HCl, can be used to prepare $ReOBr_3(SbPh_3)_2$, yield 84%.

Table I. Electrochemical and Spectroscopic Properties of Dirhenium Octahydride Complexes

complex	CV half-wave potentials, V[a]		^{1}H NMR, δ[c]			^{31}P{^{1}H}NMR, δ[c]
	$E_{p,a}$	$E_{1/2}$(ox)[b]	Re–H[d]	$-CH_3$[e]	$-CH_2-$	
$Re_2H_8(PPh_3)_4$	+0.60	−0.20 (120)[f]	−5.01 p (8.0)[g]			+42.3 s[f]
$Re_2H_8(AsPh_3)_4$	+0.70	−0.15 (130)[h]	−5.86 s			
$Re_2H_8(SbPh_3)_4$	+0.89	+0.05 (130)[i]	−6.88 s			
$Re_2H_8(PMe_2Ph)_2(PPh_3)_2$	+0.57	−0.26 (130)	−5.66 p (10.0)	+1.54 d		+43.2 s, −7.6 s
$Re_2H_8(PMe_2Ph)_2(AsPh_3)_2$	+0.51	−0.24 (90)	−6.07 t (8.5)	+1.65 d		−10.8 s
$Re_2H_8(PMe_2Ph)_2(SbPh_3)_2$	+0.66	−0.15 (140)	−6.56 t (8.8)	+1.80 d		
$Re_2H_8(PEt_2Ph)_2(PPh_3)_2$	+0.54	−0.29 (140)	−5.80 p (8.0)	+0.80 dt	+1.64 m, +1.44 m	
$Re_2H_8(PEt_2Ph)_2(AsPh_3)_2$	+0.75	−0.29 (150)	−6.24 t (10.0)	+0.92 dt	+1.72 m	
$Re_2H_8(PEt_2Ph)_2(SbPh_3)_2$	+0.66	−0.16 (140)	−6.76 t (8.8)	+0.94 dt	+1.87 m	
$Re_2H_8(PMePh_2)_3(AsPh_3)$	+0.62	−0.23 (130)	−5.80 q (9.2)	+1.88 d, +1.80 d		+15.6 s, +10.2 s
$Re_2H_8(PMePh_2)_3(SbPh_3)$	+0.69	−0.20 (150)	−6.10 q (9.6)	+1.94 d, +1.86 d		
$Re_2H_8(PEtPh_2)_3(AsPh_3)$	+0.58	−0.25 (90)	−5.91 q (9.5)	+1.00 dt	+2.05 m	
$Re_2H_8(PEtPh_2)_3(SbPh_3)$	+0.66	−0.19 (150)	−6.21 q (9.4)	+1.02 m	+2.00 m	

[a] Versus Ag/AgCl. Recorded on solutions in 0.1 M TBAH/CH_2Cl_2 by the use of a Pt-bead electrode. Data obtained at v = 200 mV s^{-1}. [b] Numbers in parentheses are ΔE_p (i.e., $E_{p,a} - E_{p,c}$) in mV. [c] NMR spectra recorded in C_6D_6. Abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. [d] $^2J_{PH}$ coupling constants (in Hz) given in parentheses (±0.5 Hz). [e] For the PMe_2Ph and $PMePh_2$ complexes these resonances are doublets with $^2J_{PH} \simeq$ 8–9 Hz, whereas for the PEt_2Ph and $PEtPh_2$ derivatives the spectra appear as doublets of triplets. [f] Data taken from ref 24. [g] Data taken from ref 18b. [h] Excellent agreement with data for a sample of this complex prepared by an alternative method.[5b] [i] The value for this couple is approximate since $i_{p,a} > i_{p,c}$; the values of $E_{p,a}$ and $E_{p,c}$ are +0.11 and −0.02 V, respectively.

Table II. Comparison of Chemical Shift Values for the Re–*H* Resonances of $Re_2H_8(EPh_3)_4$

E	δ		
	in CS_2	in CD_2Cl_2	in C_6D_6
P	−5.75[a]	−5.6[b]	−5.01[c]
As	−6.7[d]		−5.86[e]
Sb		−7.65[e]	−6.88[e]

[a] Data from: Allison, J. D.; Cameron, C. J.; Wild, R. E.; Walton, R. A. *J. Organomet. Chem.* **1981**, *218*, C62. [b] Data from ref 21. [c] Data from ref 18b. [d] Data from ref 5b. [e] This work.

The electrochemical and spectroscopic properties of $Re_2H_8(AsPh_3)_4$ and $Re_2H_8(SbPh_3)_4$ are presented in Table I. Data for the arsine complex resemble closely that reported previously.[5b] In Table II, a comparison is made between the ^{1}H NMR chemical shifts of the Re–*H* resonances as a function of NMR solvent. The considerable shift that occurs upon changing the solvent led us to use the same solvent (C_6D_6) whenever possible in all subsequent NMR spectral characterizations of the mixed-ligand complexes discussed below.

As an interesting aside, we note that the reaction of $Re_2H_8(AsPh_3)_4$ with HCl(g) in diethyl ether affords a light green precipitate, which we formulate as $Re_2Cl_6(AsPh_3)_2$ on the basis of the similarity of its IR (Nujol mull) and solid-state electronic absorption spectra to those of an "authentic" sample of $Re_2Cl_6(AsPh_3)_2$ which had been prepared previously by the reaction of β-$ReCl_4$ with $AsPh_3$ in acetone.[33] We plan to explore further the chemical reactivity of $Re_2H_8(EPh_3)_4$ (E = As, Sb).

(b) Synthesis and Characterization of $Re_2H_8(PR_2Ph)_2(EPh_3)_2$ and $Re_2H_8(PRPh_2)_3(EPh_3)$. Complexes of these types were prepared according to eqs 2 and 3 in Scheme I, with the use of the preformed dirhenium complexes $Re_2Cl_6(PR_2Ph)_2$ and $Re_2Cl_5(PRPh_2)_3$ (R = Me, Et)[25,31] as starting materials. This strategy requires that the coordinated ligands PR_2Ph and $PRPh_2$ not be labile to any significant extent in the presence of added EPh_3. This procedure works well for the complexes shown in Scheme I, but when $Re_2Cl_5(PRPh_2)_3$ was reacted with PPh_3, mixtures were obtained, and we were unable to purify the $Re_2H_8(PRPh_2)_3(PPh_3)$ that was undoubtedly present. The same was true in the case of the reactions between $Re_2Cl_6(PPh_3)_2$, $AsPh_3$ (or $SbPh_3$), and $NaBH_4$. Once again, mixtures were obtained; in the case of the phosphine–arsine system there was NMR spectroscopic evidence that several products of the type $Re_2H_8(PPh_3)_{4-n}(AsPh_3)_n$ were present, signifying that the reaction course was complicated by the occurrence of ligand exchange. It seems that this synthetic method works best when the basicity difference between the two types of ligands is greatest, although steric factors may also play a role.

An alternative approach to the synthesis of such complexes, by mixing $Re_2H_8(PR_3)_4$ with $Re_2H_8(PR'_3)_4$ etc. in the correct stoichiometric proportions, was not successful. We have shown previously that mixtures of $Re_2H_8(PMe_3)_4$ and $Re_2H_8(PMe_2Ph)_4$ do not give $Re_2H_8(PMe_3)_2(PMe_2Ph)_2$,[24] and in the present study, we found that mixtures of $Re_2H_8(PPh_3)_4$ and $Re_2H_8(PMe_2Ph)_4$ remained unchanged (as monitored by ^{1}H NMR spectroscopy).

The microanalytical data for the complexes are consistent with their formulation as dihydrates, a conclusion that is also supported by IR spectroscopy. This conclusion is reasonable given the propensity of dirhenium octahydride complexes to incorporate lattice solvent molecules[2] and the ability of other rhenium polyhydrides to form hydrates, e.g. $ReH_7(PMe_3)_2{\cdot}H_2O$.[24]

Details of the electrochemical and NMR spectral properties of these mixed-ligand complexes are listed in Table I while the 200-MHz ^{1}H NMR spectra of $Re_2H_8(PMe_2Ph)_2(EPh_3)_2$ are shown in Figure 1. All the complexes show characteristic ν(Re–H) modes in their IR spectra in the region between 2000 and 1900 cm^{-1}; these features are not especially diagnostic of any particular type of complex.[34] The cyclic voltammetric (CV) properties of solutions of these complexes in 0.1 M TBAH/CH_2Cl_2 (Table I) are typical of dirhenium octahydrides.[5b,24] They consist of a reversible couple at $E_{1/2} \simeq -0.2$ V, which corresponds to an oxidation of the bulk complex, and an irreversible oxidation at potentials greater than +0.5 V vs Ag/AgCl. The couple $E_{1/2}$(ox) shifts to increasingly more positive potentials in the order $PPh_3 < AsPh_3 < SbPh_3$, reflecting an increase in basicity of these ligands in the opposite order $SbPh_3 < AsPh_3 < PPh_3$.

The 200-MHz ^{1}H NMR spectra of solutions of the complexes in C_6D_6 consists of binomial pentets, quartets, or triplets depending upon the number of phosphine ligands (four, three, or two) that are bound to the dirhenium core. The $^2J_{PH}$ coupling constants of 8–10 Hz are typical for such fluxional octahydrides in which all of the hydride ligands are moving rapidly between bridging and terminal sites in a structure of the type $Re_2(\mu\text{-}H)_4H_4L_4$ (L represents a monodentate neutral donor ligand).[4,24] The chemical shifts for the Re–*H* resonances of the complexes listed in Table I are in all cases equal to the weighted average of the resonances of the component tetrakis(phosphine), -(arsine), and -(stibine) complexes.[24,35] For the complexes $Re_2H_8(PMe_2Ph)_2(EPh_3)_2$, the

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(33) Walton, R. A. *Inorg. Chem.* **1971**, *10*, 2534.

(34) For example: $Re_2H_8(PMe_2Ph)_2(PPh_3)_2$ 1996 (w), 1963 (m–w), 1940 (m–w) cm^{-1}; $Re_2H_8(PMe_2Ph)_2(SbPh_3)_2$ 1942 (w), 1903 (m) cm^{-1}; $Re_2H_8(PEt_2Ph)_2(AsPh_3)_2$ 1962 (m–s, br) cm^{-1}.

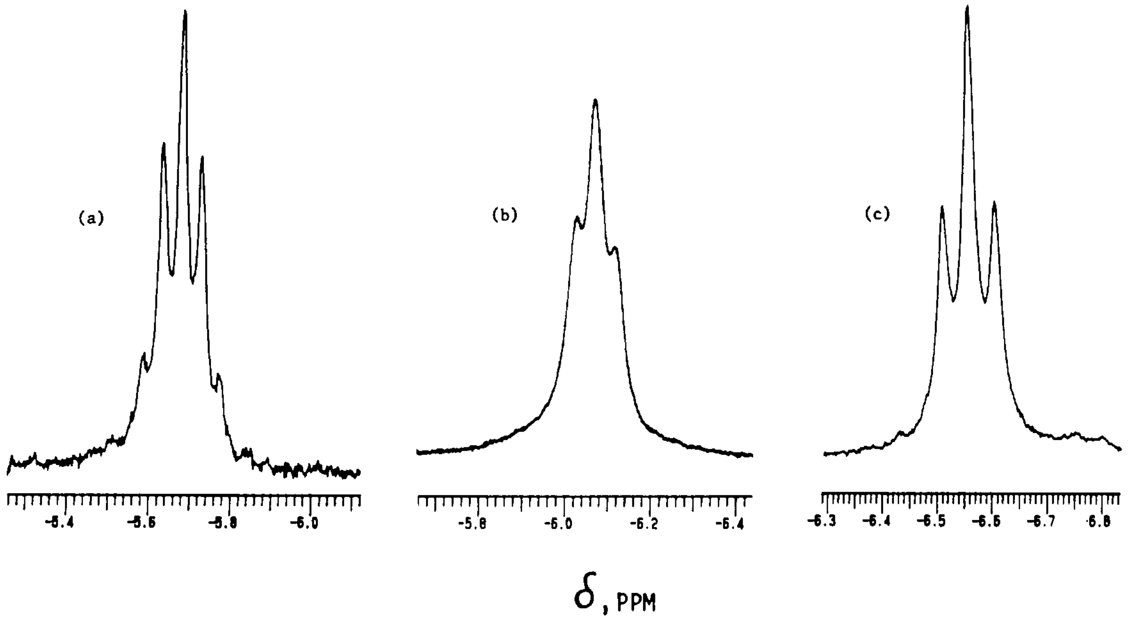

Figure 1. 200-MHz ^1H NMR spectra (recorded in C_6D_6) of $Re_2H_8(PMe_2Ph)_2(EPh_3)_2$ showing Re–*H* resonances: (a) E = P; (b) E = As; (c) E = Sb.

relative intensities of the P–CH_3 and Re–*H* resonances were in excellent agreement with the expected stoichiometric ratio of 3:2.

In the ^1H NMR spectra of $Re_2H_8(PMePh_2)_3(EPh_3)$ (E = As, Sb), the P–CH_3 resonances were observed as two sets of doublets in an intensity ratio of 2:1. This accords with a structure in which two $PMePh_2$ ligands are bound to one metal and one PMe_2Ph and one EPh_3 ligand are bound to the other metal; i.e., the disposition of phosphine ligands as present in $Re_2Cl_5(PMePh_2)_3$ is preserved. The spectrum of $Re_2H_8(PMePh_2)_3(AsPh_3)$ was recorded (in CD_2Cl_2) over the temperature range +25 to −100 °C; little change was observed upon varying the temperature. These results imply that while the hydride ligands are fluxional, the phosphine (and arsine and stibine) ligands are not undergoing exchange. In support of this, we note that the $^{31}P\{^1H\}$ NMR spectrum of $Re_2H_8(PMePh_2)_3(AsPh_3)$ shows two singlets (δ +15.6 and δ +10.2) in an intensity ratio of 2:1. A similar measurement of the $^{31}P\{^1H\}$ NMR spectrum of $Re_2H_8(PMe_2Ph)_2(PPh_3)_2$ shows two singlets of equal intensity at δ +43.2 and δ −7.6 (Table I); the former is due to the PPh_3 ligand while the latter is due to PMe_2Ph.[36] Note that the $^{31}P\{^1H\}$ NMR spectrum of $Re_2H_8(PMe_2Ph)_4$ has a singlet at δ −8.1.[24] For $Re_2H_8(PMe_2Ph)_2(PPh_3)_2$ and other complexes of the type $Re_2H_8(PR_2Ph)_2(EPh_3)_2$, it is likely that each Re atom is coordinated by one PR_2Ph and one EPh_3 ligand; however, since several isomeric forms are possible, we do not know which one has been isolated in each case.[37]

(c) Concluding Remarks. We have demonstrated that the strategy outlined in Scheme I works well for the synthesis of $Re_2H_8(PR_2Ph)_2(EPh_3)_2$ (R = Me, Et; E = P, As, Sb) and $Re_2H_8(PRPh_2)_3(EPh_3)$ (R = Me, Et; E = As, Sb). This procedure should work for other mixed-ligand systems; it requires that the appropriate $Re_2Cl_6(PR_3)_2$ and $Re_2Cl_5(PR_3)_3$ precursors be available and that the phosphine ligands which are already bound to the dirhenium core (in the aforementioned chloride complexes) not be labile. While these complexes probably have the structures $(Ph_3E)(PhR_2P)H_2Re(\mu\text{-}H)_4ReH_2(PR_2Ph)(EPh_3)$ and $(Ph_2RP)_2H_2Re(\mu\text{-}H)_4ReH_2(PRPh_2)(EPh_3)$ in the solid-state, the fluxional nature of the hydride ligands in solution prevents us from drawing any further structural conclusions at this time.

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(35) As an example, consider $Re_2H_8(PPh_3)_4$ and $Re_2H_8(PMe_2Ph)_4$, for which δ = −6.22 and δ = −5.01, respectively. Thus, the calculated value for $Re_2H_8(PMe_2Ph)_2(PPh_3)_2$ is δ −5.62, which is in excellent agreement with the experimental value of δ −5.66. Similarly, with δ −5.8 and δ −6.88 for $Re_2H_8(PMePh_2)_4$ and $Re_2H_8(SbPh_3)_4$, respectively, we calculate δ −6.07 for $Re_2H_8(PMePh_2)_3(SbPh_3)$; the experimental value is δ −6.10.

(36) We see no resolvable P–P′ coupling in any of these $^{31}P\{^1H\}$ NMR spectra. Since structure determinations on complexes of the type $Re_2H_8(PR_3)_4$ (PR_3 represents a monodentate phosphine) have shown that the P–Re–P angles are close to 105°, we are obviously dealing with a "cis" disposition of phosphine ligands for which *J*(P,P′) can be expected to be small. We find little evidence for measurable P–P′ coupling being transmitted via the Re–Re "bond".

(37) The individual $[Re(PR_2Ph)(EPh_3)]$ units can be eclipsed or staggered with respect to one another;[2] in the former case, the "planar" $(Ph_3E)(PhR_2P)Re\text{–}Re(PR_2Ph)(EPh_3)$ unit can exist with the PR_2Ph ligands in cis or trans dispositions to one another.

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Superexchange Coupling Mediated by Carboxylate and Hydrogen Bridges in Copper Amino Acid Complexes

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The study of the exchange interaction between metal centers occupies a crossing point between the search for magnetic materials and the elucidation of the role of polymetallic sites in proteins. In the first subject, many efforts have been made studying the orbital mechanisms of the exchange interactions in order to design polymetallic systems with predictable magnetic properties.[1,2] Several successes have been achieved in this direction.[3] On the other subject, the relation between the matrix elements for electron transfer and the magnetic exchange splitting (*J*) has been pointed out[4] and can be obtained from Anderson's model for superexchange[5] or with the simpler expression of Hay et al.[1] for exchange-coupled dimers. In this work we analyze magneto-structural correlations in copper amino acid complexes ($Cu(aa)_2$), in order to learn about the effectiveness and possible interferences

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