is irradiated at the boron-11 resonance frequency, a broad doublet appears at τ 9.99 (J_{PH_B} = 4.9 Hz) (Figure 1a). It arises from spin-coupling of each ^{31}P atom with the ^1H atoms of its associated BH_2 group.

The proton spin-decoupled carbon-13 NMR spectrum is a triplet (δ 66.2 with respect to Me_4Si). It is qualitatively similar to the proton NMR spectrum of the methyl hydrogens and is believed to arise from virtual coupling between ^{13}C and ^{31}P nuclei. The separation of adjacent peaks is 18.4 Hz.

A broad featureless resonance is observed in the phosphorus-31 NMR spectrum of $B_2H_4{\cdot}2P(CH_3)_3$ (δ 3.2 with respect to 85% H_3PO_4). Irradiation at the proton resonance frequency results in partial resolution of the resonance into a doublet with maxima separated by 24 Hz. This doublet is believed to result from spin-coupling of the magnetically nonequivalent (but symmetry equivalent) phosphorus-31 nuclei.

Experimental Section

All reactions were carried out under an inert atmosphere or in a standard Pyrex high-vacuum system. All solvents were dried over $LiAlH_4$ and distilled before use. Pentaborane(9) (Callery Chemical Co.) was fractionated through a −45 °C trap and collected at −78 °C. Trimethylphosphine was obtained in pure form by heating its silver iodide complex, which was prepared as described in the literature.[20-22] Trimethylamine (Matheson) was dried over $LiAlH_4$, and ammonia (Matheson) was dried over sodium before use. The adducts $B_5H_9{\cdot}2P(CH_3)_3$ and $B_5H_9{\cdot}2N(CH_3)_3$ were prepared from B_5H_9, $P(CH_3)_3$, and $N(CH_3)_3$ as described in the literature.[12] All other chemicals were reagent grade and were used without further purification.

Proton nuclear magnetic resonance (^1H NMR) spectra were taken at 100 MHz on a Varian HA-100 spectrometer. Chemical shifts are expressed in τ units with τ_{Me_4Si} = 10.00. Spin-decoupling was accomplished with a General Radio Company 1164-A coherent decade frequency synthesizer, a Hewlett-Packard 230B tuned rf power amplifier, and an Electronic Navigation Industries 3100L rf power amplifier. Boron-11 NMR spectra were recorded at 32.1 MHz on a Varian HA-100 spectrometer. The phosphorus-31 NMR spectrum was recorded at 36.4 MHz on a Bruker HX-90 spectrometer, while the carbon-13 NMR spectrum was recorded at 20.1 MHz on a Bruker WP-80 spectrometer operated in the FT mode.

Infrared spectra were obtained in CCl_4 solution on a Perkin-Elmer 457 spectrophotometer using a KBr cell. All samples were prepared in an inert atmosphere.

X-ray powder data were collected using a Debye-Scherer 114.6-mm diameter powder camera with a nickel filter and Cu Kα radiation at a wavelength of 1.54 Å. Powdered samples were scaled in 0.3-mm X-ray capillaries, under inert-atmosphere conditions.

Preparation of $B_2H_4{\cdot}2P(CH_3)_3$. In a typical reaction, 10 mmol of B_5H_9 and 30 mmol of $P(CH_3)_3$ were dissolved in 10 mL of toluene on the vacuum line and stirred for 24 h at room temperature. The solvent was removed under vacuum at 0 °C. The residue was warmed to room temperature and fractionally sublimed through a water-cooled condenser and a −78 °C trap. The $B_2H_4{\cdot}2P(CH_3)_3$ collected in the condenser, whereas the more volatile $(CH_3)_3P{\cdot}BH_3$ passed into the −78 °C trap. A yellow, syrupy residue of variable composition was left behind in the reaction vessel. The ^{11}B NMR spectrum of the residue consists of a very broad resonance centered at 48.9 ppm upfield of $BF_3{\cdot}O(C_2H_5)_2$. The ^1H NMR spectrum is a complex multiplet centered near τ 9. Hydridic hydrogen and boron were found to be in the ratio 9.2 H to 2.0 B.

A typical yield of $B_2H_4{\cdot}2P(CH_3)_3$ from reaction conditions described above was about 7 mmol (70% yield based upon 1 B_5H_9 yielding 1 $B_2H_4{\cdot}2P(CH_3)_3$). Yields were markedly diminished at temperatures above room temperature.

Hydrolysis of $B_2H_4{\cdot}2P(CH_3)_3$ in 6 M hydrochloric acid over a period of several days yielded 3.92 mol of hydrogen/mol of compound. The resulting hydrolyzate was found to reduce silver ion to metallic silver, which indicated that a boron–boron bond was present in the molecule. Hydrolysis with aqueous KOH on a fresh sample of adduct produced 5.1 mol of hydrogen gas/mol of compound. As basic hydrolysis is known to be quite effective in cleaving boron–boron bonds, the extra mole of hydrogen given off resulted from the rupture of this boron–boron bond.[23] Base hydrolysis in D_2O gave hydrogen gas with an HD–D_2 ratio of 4:1.

Anal. Calcd for $C_6H_{22}B_2P_2$: B, 12.1; hydridic H, 2.3; mol wt 117.6. Found: B, 11.9; hydridic H, 2.2; mol wt (cryoscopic, benzene solution) 181.

Infrared spectrum of $B_2H_4{\cdot}2P(CH_3)_3$ (CCl_4 solution) (cm^{-1} (relative intensity)): 2990 (vs), 2910 (vs), 2410 (sh), 2370 (sh), 2310 (vs), 2200 (w), 1430 (vs), 1415 (vs), 1288 (vs), 1308 (vs), 1215 (vs), 1135 (w), 1108 (w), 1062 (m), 1030 (m), 980 (sh), 950 (vs), 921 (s), 900 (m), 850 (m), 850 (m), 700 (m), 663 (m), 640 (w), 618 (w), 546 (m).

X-ray powder diffraction pattern of $B_2H_4{\cdot}2P(CH_3)_3$ (*d*, Å (relative intensity)): 3.63 (s), 2.72 (vs), 2.57 (s), 2.41 (vs), 2.34 (m), 2.23 (m), 2.09 (s), 1.96 (m), 1.79 (w), 1.74 (vw), 1.64 (m), 1.58 (m), 1.52 (m), 1.42 (m), 1.38 (m), 1.31 (m), 1.17 (m).

Reaction of $B_5H_9{\cdot}2P(CH_3)_3$ with Lewis Bases. In a typical reaction, 5 mmol of Lewis base ($P(CH_3)_3$ or $N(CH_3)_3$) was condensed into a vessel which contained 5 mmol of $B_5H_9{\cdot}2P(CH_3)_3$ in 10 mL of toluene. The solution was stirred for 24 h at room temperature. The products consisted of borane adducts $L{\cdot}BH_3$ (L = $P(CH_3)_3$ or $N(CH_3)_3$), $B_2H_4{\cdot}2P(CH_3)_3$, and $(CH_3)_3P{\cdot}BH_3$ and a viscous, yellow, nonvolatile liquid. These materials were separated as described in the preceding section. The yield of $B_2H_4{\cdot}2P(CH_3)_3$ when the added base was $P(CH_3)_3$ was comparable (70%) to that obtained from the direct reaction of B_5H_9 with $P(CH_3)_3$ in a 1:3 molar ratio. The yield of $B_2H_4{\cdot}2P(CH_3)_3$ when $N(CH_3)_3$ was the added base was about half the yield (ca. 35%) when $P(CH_3)_3$ was the added base.

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Registry No. $B_2H_4{\cdot}2P(CH_3)_3$, 67113-98-8; B_5H_9, 19624-22-7; $P(CH_3)_3$, 594-09-2; $B_5H_9{\cdot}2P(CH_3)_3$, 39661-74-0; ^{13}C, 14762-74-4.

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Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Complex Halides of the Transition Metals. 26.[1] Reactions of the Octachlorodirhenate(III) Anion with Sodium Borohydride in the Presence of Tertiary Phosphines. Facile Routes to the Dimers $Re_2Cl_4(PR_3)_4$ and $Re_2H_8(PR_3)_4$

P. Brant and R. A. Walton*

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Sodium borohydride has found extensive application as a synthetic reagent in transition-metal chemistry. In its reactions with transition-metal complexes $NaBH_4$ most often effects

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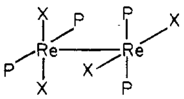
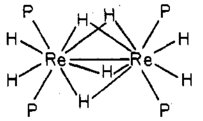
facile metal reduction[2] and/or the formation of metal–hydrido complexes.[3] We have been interested in reductions of the $Re_2X_8^{2-}$ dimers (X = Cl, Br, I) and their derivatives, in which the Re(III) atoms are joined by a quadruple ($\sigma^2\pi^4\delta^2$) bond. It was previously found[4,5] that tertiary phosphines can reduce the octahalodirhenate(III) anions, generating complexes of the types $Re_2X_5(PRPh_2)_3$ and $Re_2X_4(PR_3)_4$ (structure I).



I



II

However, these reactions require from 3 to 10 days and the extent of reduction is dependent on the basicity of the phosphine. The addition of $NaBH_4$ to these reaction mixtures presented both the possibility of much more rapid generation of reduced rhenium dimers as well as the possibility of formation of new rhenium–hydrido complexes. There have been some previous investigations of the reactions of $NaBH_4$ and $LiAlH_4$ with monomeric rhenium complexes,[3] the last being reported by Chatt and Coffey in 1969.[6] Among the products isolated were complexes of the types $ReH_5(PR_3)_3$ and $ReH_7(PR_3)_2$, as well as species which were formulated as $[ReH_x(PEt_2Ph)_2]_2$ and $[ReH_x(PPh_3)_2]_n \cdot n$(solvent). In a recent structure determination of $[ReH_x(PEt_2Ph)_2]_2$, Bau and coworkers[7] found that $x = 4$ and that the molecule consists of a planar Re_2P_4 fragment with four hydrogens bridging the two rhenium atoms and two terminal hydrido ligands bound to each rhenium atom (structure II).

We now report new pathways for the formation of the dimeric rhenium complexes $Re_2Cl_4(PR_3)_4$ and $Re_2H_8(PR_3)_4$ via reactions of the octachlorodirhenate anion with sodium borohydride in the presence of tertiary phosphines.

Experimental Section

Starting Materials. $(Bu_4N)_2Re_2Cl_8$ was prepared by the established method.[8] $NaBH_4$ was purchased from Alfa Products. The phosphine ligands PEt_3, $P(n\text{-}Pr)_3$, $PEtPh_2$, and PPh_3 were purchased from Strem Chemicals, Inc. Solvents were reagent grade and used as received.

Physical Measurements. Infrared spectra of Nujol mulls were recorded in the region 4000–200 cm^{-1} with a Beckman IR-12 spectrophotometer. A Perkin-Elmer R32 NMR spectrometer was used to obtain the NMR spectra. Samples were dissolved in C_6D_6, and peak resonances were internally referenced to Me_4Si (Mallinckrodt). Cyclic voltammetry experiments were performed with a BioAnalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x–y recorder. Potential control for coulometric experiments was maintained with a potentiostat purchased from BioAnalytical Systems, Inc. All voltammetric measurements were made on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte using a platinum-bead electrode. X-ray photoelectron spectra (XPS) were recorded using a Hewlett-Packard 5950A spectrometer. Binding energies were internally standardized to a coordinated tertiary phosphine C 1s binding energy of 285.0 eV.[9] The magnetic moment of $Re_2H_8(PPh_3)_4$ was determined by the Gouy method. The diamagnetic correction was estimated using Pascal's constants. Uncorrected melting points were determined in open capillaries with a Fischer Meltemp apparatus.

Reactions. All reactions were carried out under an atmosphere of nitrogen in deoxygenated solvents.

$Re_2Cl_4(PEt_3)_4$. In a typical reaction, 0.2 mL (1.6 mmol) of triethylphosphine was added to a stirred, refluxing solution of 0.4 g (0.365 mmol) of $(Bu_4N)_2Re_2Cl_8$ in 8 mL of ethanol. After 15 min, a solution of 0.15 g (4 mmol) of $NaBH_4$ in 5 mL of methanol was added dropwise. Considerable gas evolution ensued and the solution darkened. After the mixture was refluxed for an additional 15 min, the flask was cooled and the gray microcrystalline $Re_2Cl_4(PEt_3)_4$ was collected and washed with methanol, ethanol, and diethyl ether. $Re_2Cl_4(PEt_3)_4$ was contaminated with a white, water-soluble salt (presumably NaCl), so it was *rapidly* dissolved in dichloromethane under nitrogen, filtered, and precipitated with excess diethyl ether. Anal. Calcd for $Re_2Cl_4(PEt_3)_4$: C, 29.23; H, 6.09. Found: C, 29.87; H, 5:96; yield 0.23 g (67%).

$Re_2Cl_4(P(n\text{-}Pr)_3)_4$. A quantity of tri-*n*-propylphosphine, 0.70 mL (4.0 mmol), was added to a stirred, refluxing solution of 1.0 g (0.87 mmol) of $(Bu_4N)_2Re_2Cl_8$ in 10 mL of ethanol. After this solution was stirred for 10 min, a solution of 0.30 g (8 mmol) of $NaBH_4$ in 7 mL of methanol was added dropwise. As before, a gas evolved and the solution darkened. After the final reaction mixture was refluxed for 10 min, the flask was cooled, and the gray precipitate was isolated and washed with methanol, ethanol, and diethyl ether. The product was dissolved in a minimum of benzene under N_2, filtered to remove a white salt impurity, and precipitated as gray microcrystals with petroleum ether. Anal. Calcd for $Re_2Cl_4(P(n\text{-}Pr)_3)_4 \cdot 0.5C_6H_6$: C, 39.27; H, 7.29. Found: C, 38.91; H, 6.84; yield 0.57 g (57%). Further evidence in support of the presence of "lattice" benzene was provided by NMR spectroscopy.

$Re_2Cl_4(PEtPh_2)_4$ and $Re_2H_8(PEtPh_2)_4$. Ethyldiphenylphosphine, 0.35 mL (1.5 mmol), was added to a suspension of 0.40 g (0.35 mmol) of $(Bu_4N)_2Re_2Cl_8$ in 12 mL of ethanol. The mixture was refluxed for 5 min and then a solution of 0.10 g (2.6 mmol) of $NaBH_4$ in 5 mL of methanol was added dropwise. Considerable frothing resulted and the solution turned dark brown. After refluxing an additional 5 min, the solution was cooled to room temperature and the light brown precipitate isolated by filtration. The resulting complex $Re_2Cl_4(PEtPh_2)_4$ was separated from a white, water-soluble salt by washing the precipitate with benzene. A mixture of petroleum ether–*n*-hexane (1:1 by volume) was added to the benzene filtrate to force precipitation of the light brown $Re_2Cl_4(PEtPh_2)_4$. This product was filtered, washed with *n*-hexane, and dried in vacuo. Anal. Calcd for $Re_2Cl_4(PEtPh_2)_4 \cdot 0.5C_6H_6$: C, 50.25; H, 4.47; P, 8.79. Found: C, 50.80; H, 4.75; P, 8.87; yield 0.24 g (46%). The presence of "lattice" benzene in this product was confirmed by NMR spectroscopy. The ethanol–methanol solvent was removed from the filtrate under reduced pressure, and the remaining red gummy oil was further dried in vacuo for 0.5 h. The oil was dissolved in 5 mL of tetrahydrofuran followed by 15 mL of hexane–petroleum ether (1:1 by volume). A small quantity of a white crystalline uncharacterized solid precipitated from the solution when it was allowed to stand at 0 °C for 12 h. This solid was removed and the volume of the filtrate was reduced to ~5 mL at which time the red-brown complex $Re_2H_8(PEtPh_2)_4$ precipitated. It was isolated, washed with hexane, dried, and finally recrystallized from benzene. Anal. Calcd for $Re_2H_8(PEtPh_2)_4$: C, 54.37; H, 5.50. Found: C, 55.48; H, 5.30; yield 0.14 g (32%).

$Re_2H_8(PPh_3)_4$. In a typical reaction, a solution of 0.13 g of $NaBH_4$ (3.5 mmol) in 5 mL of methanol was added *dropwise* to a refluxing stirred mixture of $(Bu_4N)_2Re_2Cl_8$ (0.20 g; 0.17 mmol) and triphenylphosphine (0.28 g; 1.07 mmol) in ethanol. Considerable frothing resulted and the color of the mixture changed from green to red brown. The mixture was refluxed for an additional 5 min and then cooled to room temperature. The dark red brown precipitate was collected and washed with 10 mL of hot ethanol, 10 mL of hot methanol, 15 mL of acetone, and 10 mL of hexane, leaving the red product. Anal. Calcd for $Re_2H_8(PPh_3)_4 \cdot MeOH$: C, 60.10; H, 4.93; P, 8.6. Found: C, 60.42; H, 5.20; P, 9.24; yield 30%.

Results and Discussion

Previously, the reduced complexes $Re_2Cl_4(PR_3)_4$ could be formed in several days by direct reaction of the appropriate tertiary phosphine with $(Bu_4N)_2Re_2Cl_8$ in refluxing acetone or ethanol.[4] It is now possible to isolate the same complexes in less than 1 h by addition of excess $NaBH_4$ to the reaction mixture, and the yields (~50–75%) are comparable with those obtained employing the former method. In addition, the new Re(II) dimer $Re_2Cl_4(PEtPh_2)_4$ can be prepared in fairly good yield (47%) via $NaBH_4$ reduction. Reaction of $PEtPh_2$ with $(Bu_4N)_2Re_2Cl_8$ in the absence of $NaBH_4$ results only in the formation of $Re_2Cl_5(PEtPh_2)_3$.[4] This phosphine is not sufficiently basic enough to reduce $Re_2Cl_8^{2-}$ to $Re_2Cl_4(PEtPh_2)_4$ in the absence of $NaBH_4$. The colors, elemental analyses, infrared and X-ray photoelectron spectra, and electrochemical data for $Re_2Cl_4(PEt_3)_4$ and $Re_2Cl_4(P(n\text{-}Pr)_3)_4$ are in excellent agreement with the published data for these compounds.[4,10,11] The new dimer $Re_2Cl_4(PEtPh_2)_4$ exhibits properties which are

Table I. Properties of Rhenium Dimers Containing Metal-Metal Triple Bonds

complex	mp	color	IR absorptions, cm^{-1}		XPS, eV[a]		
			ν_{Re-H}	ν_{Re-Cl}	Re $4f_{7/2}$	Cl $2p_{3/2}$	P $2p_{3/2}$
$Re_2Cl_4(PEtPh_2)_4$	127–128 dec	tan		332 s, 308 m	41.5 (1.2)	198.7 (1.3)	131.3 (1.4)
$Re_2H_8(PEtPh_2)_4$	153–154 dec	red	1994 m, 1922 m		40.4 (1.5)		131.0 (1.4)
$Re_2H_8(PPh_3)_4 \cdot MeOH$	161–163 dec	red	2010 vw, 1990 vw		40.9 (1.5)		131.3 (1.3)

complex	^1H chemical shifts, δ[b]				
	alkyl				
	α	β	γ	phenyl	hydride
$Re_2Cl_4(PEt_3)_4$	2.28 br	1.04 p [$J_{CH_3-P} = 14$, $J_{CH_3-CH_2} = 7$]			
$Re_2Cl_4(P(n\text{-}Pr)_3)_4$	2.32 br	1.45 br	0.96 t [$J_{CH_3-CH_2} = 7$]		
$Re_2Cl_4(PEtPh_2)_4$	2.24 br	0.80 br		7.08 (1.6); 7.90 (1.0)	
$Re_2H_8(PEtPh_2)_4$	2.25 br	1.10 br		7.00 (4.5); 8.06 (1.0)	−8.05 br

[a] Full-width at half-maximum values (fwhm) given in parentheses; binding energies referenced to a C 1s binding energy of 285.0 eV for the phosphine ligands. [b] Abbreviations are as follows: br = broad, p = pentet, t = triplet. Coupling constants, *J*, are in Hertz. Relative peak areas of phenyl resonances are given in parentheses.

characteristic of the $Re_2Cl_4(PR_3)_4$ series. These properties are summarized in Table I. Specifically, the XPS Re $4f_{7/2}$ binding energy and the two reversible electrochemical one-electron (by coulometry) oxidations at −0.29 and +0.84 V are in the ranges observed for Re(II) dimers of this type.[10,11] Also observed in the cyclic voltammograms of $Re_2Cl_4(PEtPh_2)_4$, is a weak reversible wave at +0.44 V due to the formation of trace amounts of $Re_2Cl_5(PEtPh_2)_3$. Such weak reversible waves due to $Re_2Cl_5(PR_3)_3$ are usually observed in the cyclic voltammograms of other Re(II) dimers of this type.[11]

Just as the extent of direct phosphine reduction of the $Re_2Cl_8^{2-}$ anion is determined by the number of phenyl substituents in the tertiary phosphine, so the products obtained in the borohydride reduction of $(Bu_4N)_2Re_2Cl_8$ are partitioned between $Re_2H_8(PPh_3)_4$ and $Re_2Cl_4(PR_3)_4$ according to the phosphine used. When a methanolic $NaBH_4$ solution is added to a mixture of $(Bu_4N)_2Re_2Cl_8$ and PPh_3, the sole product isolated is the orange or brick red methanol solvate of $Re_2H_8(PPh_3)_4$, there being no evidence for the formation of $Re_2Cl_4(PPh_3)_4$. The insolubility of the methanol solvate prevented us from investigating the solution properties of this complex.

However, if one phenyl group in triphenylphosphine is exchanged for an alkyl group, as in ethyldiphenylphosphine, the products of the reduction of $(Bu_4N)_2Re_2Cl_8$ by $NaBH_4$ are $Re_2Cl_4(PEtPh_2)_4$ and $Re_2H_8(PEtPh_2)_4$ in a molar ratio of ~1.5:1.0. In the case of reduction of $(Bu_4N)_2Re_2Cl_8$ by $NaBH_4$ in the presence of trialkylphosphines, the sole product we isolated was $Re_2Cl_4(PR_3)_4$.

The $Re_2H_8(PR_3)_4$ complexes were previously prepared[6] by the following route:

$$ReOCl_3(PR_3)_2 + LiAlH_4 \xrightarrow{THF} \underset{\mathbf{1}}{ReH_7(PR_3)_2} + \underset{\mathbf{2}}{Re_2H_8(PR_3)_4} \quad (PR_3 = PEt_2Ph \text{ or } PPh_3)$$

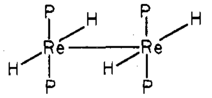
The product obtained, **1** or **2**, is dependent on the conditions of the reaction, with **1** being converted into **2** by heat.[6] The identity of the $Re_2H_8(PPh_3)_4 \cdot MeOH$ obtained by the $NaBH_4$ reduction of $(Bu_4N)_2Re_2Cl_8$ in the presence of triphenylphosphine was verified by comparison of its color, characteristic infrared band (ν_{Re-H} at 2010 (vw) and 1990 (vw) cm^{-1} and ν_{O-H} of lattice MeOH at ~3540 cm^{-1}), and melting point with the previously reported data,[6] as well as by its elemental analyses. $Re_2H_8(PEtPh_2)_4$ has not been previously synthesized. It is baffling to note that in the reaction of $ReOCl_3(PR_3)_2$ with $LiAlH_4$, either **1** or **2** could be isolated when the tertiary phosphine used was PEt_2Ph or PPh_3, but the sole product when $ReOCl_3(PEtPh_2)_2$ was employed was $ReH_7(PEtPh_2)_2$.[6] The infrared spectrum of $Re_2H_8(PEtPh_2)_4$ shows two rhenium–hydride stretching frequencies of moderate intensity at 1994 and 1922 cm^{-1}. A broad hydride resonance was found in the NMR spectrum at δ −8.05. Integrated intensities yielded a phosphine:hydride molar ratio of 1:1.75, in reasonable agreement with the expected value of 1:2. The hydride resonance observed is similar to that found for $Re_2H_8(PEt_2Ph)_4$ (δ −6.6);[6,7] however, the quintet pattern observed[6,7] in the spectrum of $Re_2H_8(PEt_2Ph)_4$ could not be resolved in the room-temperature spectrum of $Re_2H_8(PEtPh_2)_4$.

In addition to comparisons of the infrared and NMR data for $Re_2H_8(PPh_3)_4$ and $Re_2H_8(PEtPh_2)_4$, both of these octahydrido complexes were characterized by X-ray photoelectron spectroscopy (XPS). The data are summarized in Table I. Both complexes exhibit P $2p_{3/2}$ binding energies which are characteristic of coordinated tertiary phosphines. In agreement with their formulations, a Cl 2p signal could not be found. Finally, the Re $4f_{7/2}$ binding energies for the two complexes (~40.6 eV) are very low. Such low metal binding energies are characteristic of metal–hydrido complexes (cf. $ReH_5(PMe_2Ph)_3$ 40.5 eV)[12] and are due to the strong σ-donor ability of the hydrido ligand.

With the exception of the hydride resonances discussed by Chatt and Coffey[6] and also observed by Bau and co-workers[7] for $Re_2H_8(PEt_2Ph)_4$, the NMR spectra of these reduced rhenium dimers have not been reported. We were interested in obtaining NMR data for these complexes because San Filippo[13] had previously reported NMR data for the Re(III) dimers $Re_2Cl_6(PR_3)_2$ as well as for a number of isoelectronic, isostructural molybdenum dimers $Mo_2Cl_4(PR_3)_4$ and found that the spectra exhibited unusual downfield shifts of the α protons (δ ~2.15–2.44) in the alkyl substituents of the coordinated tertiary phosphines.[13] These shifts were attributed to diamagnetic anisotropic shielding of the protons due to the metal–metal quadruple bond ($\sigma^2\pi^4\delta^2$) in the complexes. It seemed probable that similar shifts might be observed in the complexes $Re_2Cl_4(PR_3)_4$ and $Re_2H_8(PR_3)_4$ which contain metal–metal triple bonds. The NMR data are presented in Table I. As the table shows, the resonances of the α protons in the alkyl substituents of the coordinated monodentate phosphines are all shifted downfield (between δ 2.24 and δ 2.32), and the shifts observed are within the range reported by San Filippo.[13] The presence of a single resonance for the α protons indicates rapid rotation of the coordinated phosphines on the NMR time scale and is consistent with the magnetically equivalent positions of the tertiary phosphines in these complexes. The downfield shift of the α-proton resonance recorded for $Re_2H_8(PEtPh_2)_4$ is consistent with the short Re–Re distance (2.54 Å) determined in the PEt_2Ph

analogue[7] and is independent evidence for the presence of multiple bonding involving the two rhenium atoms in the octahydrido complexes.

Comments Concerning the Bonding in $Re_2H_8(PR_3)_4$. The octahydrido dimers, $Re_2H_8(PR_3)_4$, can formally be considered as derivatives of Re(IV),[7] and the presence of a Re–Re triple bond follows upon applying the EAN rule. We believe that one way of viewing the bonding in these species is to consider them to be products of the hydrogenation of the rhenium(II) dimers $Re_2H_4(PR_3)_4$. Although these dimers are unknown, the halide analogues $Re_2X_4(PR_3)_4$ are well characterized.[4,14] The tetrahydrido moiety (structure III) is assigned a structure



III

which is analogous to that of the tetrahalo complexes $Re_2X_4(PR_3)_4$ (structure I),[14] with the exception that the hydrido complex is centrosymmetric while the tetrahydro dimers are noncentrosymmetric.[14] The effect of eclipsing the phosphines as in III will be to decrease the P–Re–P angle (due to increased nonbonded repulsion between the phosphine ligands of adjacent ReP_2 sets) relative to that observed in the noncentrosymmetric complex, but one might consider that the Re–Re bonding order $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ remains intact.

We prefer to consider the bonding in the hydride bridges in the following manner. There is no net bonding provided by the $(\delta)^2(\delta^*)^2$ orbital set in the Re_2^{4+} fragment of $Re_2H_4(PR_3)_4$. However, the hydride bridges in $Re_2H_8(PR_3)_4$ mix with the δ–δ^* set, and net bonding is now possible in a $Re_2(\mu\text{-H})_4^{4+}$ moiety in which the eight electrons (four from the two Re d_{xy} orbitals and four from the four hydrogen atoms) are distributed among six orbitals (arising from the two $5d_{xy}$ orbitals from the Re atoms and the four H 1s orbitals). Since the set of four orbitals which are filled will be predominantly bonding in character, while the two highest energy antibonding orbitals are empty, there will likely be a net stabilization of the $Re_2H_8(PR_3)_4$ molecules. This approach to the bonding of the octahydrido dimers raises the question as to whether the "parent" dimers $Re_2H_4(PR_3)_4$ exist. The isolation of these species is of interest both from the point of view of exploring their reactivity toward hydrogen and other molecules and as subjects for theoretical calculations (especially those of the SCF–Xα–SW type).[15] Efforts to synthesize the hydride dimers $Re_2H_4(PR_3)_4$ are currently underway in our laboratory.

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Registry No. $Re_2Cl_4(PEt_3)_4$, 55400-06-1; $Re_2Cl_4(P(n\text{-}Pr)_3)_4$, 55400-08-3; $Re_2Cl_4(PEtPh_2)_4$, 66984-39-2; $Re_2H_8(PEtPh_2)_4$, 66984-38-1; $Re_2H_8(PPh_3)_4$, 66984-37-0; $(Bu_4N)_2Re_2Cl_8$, 14023-10-0; $NaBH_4$, 16940-66-2.

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Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Preparation of a Stereospecifically ^{13}CO-Labeled $[(\mu\text{-H})[Mo(CO)_5]_2]^-$ Species and Analysis of Its CO Stretching Vibrational Modes

Donald J. Darensbourg,* Robert R. Burch, Jr.,
and Marcetta Y. Darensbourg*

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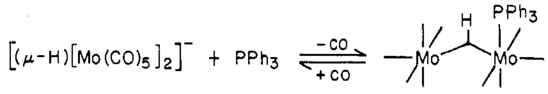
The extent to which reactive sites on metal atoms are influenced by chemically bound adjacent metal centers continues to be a perplexing problem, demanding both chemical and physical approaches. An investigation of the reactions of $[Et_4N]^+[(\mu\text{-H})[M(CO)_5]_2]^-$ (M = Cr, Mo, W) with phosphines and phosphites to afford $L_2M(CO)_4$ complexes was recently reported.[1,2] For the reaction of $[(\mu\text{-H})[Mo(CO)_5]_2]^-$ with PPh_3 it was possible to isolate an intermediate prior to dimer disruption. This asymmetric bridging hydride carbonylate (I) has been shown to contain PPh_3 in an equatorial position by single-crystal X-ray diffraction methods[3-6] as well as by infrared spectroscopy in the ν(CO) region. As is indicated in eq 1, this process is readily reversible, with dissociation of PPh_3 occurring under rather mild conditions. Thus, it has been possible to carry out the reverse reaction of eq 1 in the presence of ^{13}C-labeled carbon monoxide to afford $[(CO)_5Mo\text{–}H\text{–}Mo(CO)_4(^{13}CO)]^-$. We wish to communicate the details of the preparation of this labeled species along with an analysis of its ν(CO) infrared spectral data. The impetus for this investigation was a desire to determine whether the two $M(CO)_5$ moieties interact across the hydride bridge in such a way as to affect ν(CO).



(1)

I

Experimental Section

Preparation of $[Et_4N]^+[(CO)_5Mo\text{–}H\text{–}Mo(CO)_4(^{13}CO)]^-$. $[Et_4N]^+[(\mu\text{-H})[Mo(CO)_5][Mo(CO)_4PPh_3]]^-$ was prepared by the procedure previously described.[2] A solution of 0.060 g of $[Et_4N]^+[(\mu\text{-H})[Mo(CO)_5][Mo(CO)_4PPh_3]]^-$ in 8.0 mL of THF (distilled from Na–benzophenone) was prepared under a nitrogen atmosphere. The solution was transferred via syringe to a nitrogen-flushed tube of volume 25 mL equipped with a stopcock and serum cap at its sole outlet. A stream of ^{13}CO (>90% enriched, Prochem, BOC Ltd., London) was introduced to the solution by means of a syringe needle through the serum cap until a pressure of approximately 2 atm was attained. The reaction vessel was then placed in a constant temperature bath thermostated at 51.6 °C, and the reaction was allowed to proceed in the dark for 90 min, at which time the reaction had gone to completion as indicated by the ν(CO) infrared spectrum of the reaction mixture.

Infrared Spectra. The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a linear-absorbance

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