π-donation with a vacant metal fragment orbital in the equatorial plane and π-back-bonding with an orbital oriented in the axial direction.[17] When the system is converted to a simple square pyramid, the calculated barrier to formal rotation becomes 12 kcal mol^{-1}, reminiscent of change in the barrier for olefin rotation in d^8 $Fe(CO)_4$(olefin).[18]

We are aware of no reports concerning the synthesis of a simple four-electron monoalkyne complex of a d^6 ML_4 fragment.[19] This is remarkable considering the extensive group 6 alkyne chemistry that began with the synthesis of W(alkyne)$_3$(CO) complexes over 25 years ago.[21] The availability of reagents that are both electron rich and labile, such as the 1,5-COD complexes utilized here, is critical to the synthetic strategy for introducing excellent π-acceptor ligands, such as alkynes and 1,3-dienes.[3]

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Supplementary Material Available: Synthetic and spectroscopic data for **1a** and **1b**, details of extended Hückel calculations, and methods and results (listings) of the crystal structure study of **1a** (11 pages); listing of observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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An Unusual, Electronically Unsaturated Dirhenium Polyhydride Complex with No Metal-Metal Bond

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Many mononuclear and dinuclear mixed polyhydride–phosphine (or arsine or stibine) complexes of rhenium are known, in a variety far greater than that for any other transition element. In the case of the dirhenium species, these are of the generic types $[Re_2H_9(PR_3)_4]^+$, $Re_2H_8(PR_3)_4$, $[Re_2H_7(PR_3)_5]^+$, $Re_2H_6(PR_3)_5$, $[Re_2H_5(PR_3)_6]^+$, and $Re_2H_4(PR_3)_6$, where PR_3 represents a monodentate or one-half a bidentate phosphine.[1-14] With one exception, the structural characterizations of representative examples of these compounds have revealed the presence of three or four bridging hydrido ligands and a short Re–Re distance (2.51–2.61 Å).[2,5,8-11] The latter observation has led to the conclusion that some degree of multiple metal–metal bonding is present, represented in terms of direct Re–Re bonding and/or three-center, two-electron Re–H–Re bonds.[15,16] The single exception is the complex $Re_2(\mu\text{-}H)_2H_6(\mu\text{-dppm})_2$ (dppm = $Ph_2PCH_2PPh_2$), which contains only two bridging hydrido ligands and possesses the much longer Re–Re bond distance of 2.9335 (9) Å. We now report the isolation of a molecule, viz., $[Re_2H_5(dmpm)_3]PF_6$ (dmpm = $Me_2PCH_2PMe_2$), that takes this trend to its extreme, namely, no direct Re–Re interaction whatsoever and metal centers that are electronically unsaturated. This may presage the discovery of other compounds of this type with metals that normally show a propensity to form strong metal–metal interactions.[17]

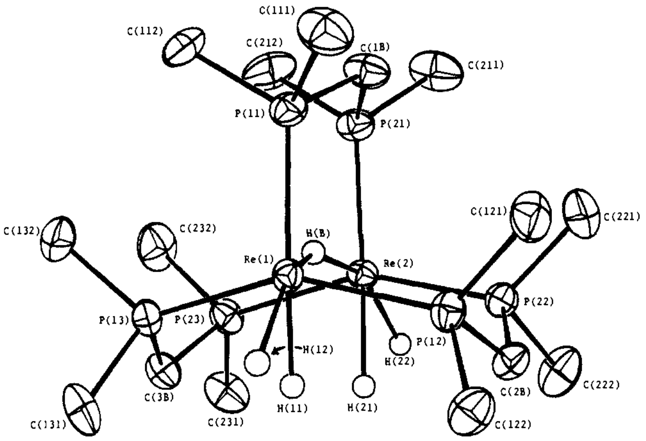

Figure 1. ORTEP view of the structure of the $[Re_2H_5(dmpm)_3]^+$ cation with the hydrogen atoms of the dmpm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level, except for the hydride ligands, which are circles of arbitrary radius. Some representative and important bond distances (Å) and angles (deg) and torsional angles (deg) are as follows: Re(1)–P(11) = 2.408 (2), Re(1)–P(12) = 2.365 (2), Re(1)–P(13) = 2.371 (2), Re(1)–H(B) = 1.53 (7), Re(1)–H(11) = 1.64 (8), Re(1)–H(12) = 1.7 (1), Re(2)–H(B) = 2.06 (7); Re(2)–Re(1)–P(11) = 85.48 (4), Re(2)–Re(1)–H(11) = 76 (3), Re(2)–Re(1)–H(12) = 135 (3), P(11)–Re(1)–H(12) = 139 (3), P(11)–Re(1)–P(12) = 102.73 (7), P(12)–Re(1)–P(13) = 151.07 (6); Re(1)–H(B)–Re(2) = 156 (5); P(11)–Re(1)–Re(2)–P(21) = 0.30 (7), P(12)–Re(1)–Re(2)–P(22) = 2.34 (7), P(13)–Re(1)–Re(2)–P(23) = 1.69 (7). Distances involving Re(2) are similar to those for Re(1) and, therefore, are not listed here.

The reaction of the triply bonded dirhenium(II) complex $Re_2Cl_4(\mu\text{-dmpm})_3$[18] (0.453 g, 0.49 mmol) with $LiAlH_4$ (0.32 g, 8.4 mmol) in THF (20 mL) at room temperature afforded a green solution. The mixture was stirred for 2 h, hydrolyzed with 20 mL of a H_2O/THF (5:15 mL) mixture, and then heated gently. After

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2 h, the resultant yellow solution was filtered, the filtrate evaporated to dryness, and the residue dissolved in 5 mL of water. Addition of a stoichiometric amount of KPF_6 (0.099 g, 0.54 mmol) dissolved in 1 mL of water yielded the complex as a yellow solid. This product was washed with water and diethyl ether and dried under vacuum; yield 0.342 g (75%).

Solutions of the complex in CD_2Cl_2 show an uncomplicated ^1H NMR spectrum (at +20 °C), with methyl and methylene resonances appearing as broad singlets at δ +1.82 and +2.98, respectively, and a binomial septet at δ −8.42 (J_{HP} = 9.2 Hz) due to the hydride ligands coupled to six equivalent phosphorus atoms (Figure S1 in the supplementary material). This behavior is characteristic of a fluxional rhenium polyhydride complex. When these solutions are cooled to −100 °C, the Re*H* resonance broadens and approaches coalescence but we were unable to obtain the spectrum of the limiting static structure. Likewise, the P*Me* resonance broadened slightly but otherwise remained unchanged as the temperature was lowered. The $^{31}P\{^1H\}$ spectrum (recorded in CD_2Cl_2 at +20 °C) displays a singlet at δ −28.7 for the dmpm phosphorus atoms; this signal was also a singlet in ca. −80 °C. A selective 2DJ ^{31}P NMR experiment (Figure S1) shows the dmpm phosphorus resonance split into six peaks (J_{HP} = 9.2 Hz). This confirms the presence of five hydride ligands in the complex.

The X-ray crystal structure of $[Re_2H_5(dmpm)_3]PF_6$ was determined on a crystal grown from 1,2-dichloroethane/diisopropyl ether.[19-21] The key features of the structure of the $[Re_2H_5(dmpm)_3]^+$ cation are shown in Figure 1. While this species possesses no crystallographically imposed symmetry, it approximates C_s symmetry with the mirror plane encompassing the carbon atoms of the CH_2 groups of the three dmpm ligands and bisecting the Re–Re vector. The Re_2P_6 skeleton is essentially eclipsed. The most remarkable feature in this structure is the very long Re–Re distance of 3.5150 (4) Å, which clearly accords with the absence of any direct Re–Re bonding. We can view the structure as arising formally from the protonation of the neutral species $Re_2H_4(dmpm)_3$, in which the individual Re atoms have 15-electron counts, such that a three-center, two-electron Re–H–Re bonding interaction gives rise to a diamagnetic ground state. This structure differs from those of all other $[Re_2H_5]^+$ species that have been structurally characterized,[9-11] in which there is a $[HRe(\mu\text{-}H)_3ReH]$ unit and a very short Re–Re distance (2.58–2.60 Å). This $[Re_2H_5(dmpm)_3]^+$ structure likely represents one structural extreme in the series of terminal/bridging Re–H bond forming/breaking processes that presumably account for the fluxionality of this complex in solution.

The terminal Re–H bond lengths (1.6–1.8 (1) Å) are normal for M–H distances determined by X-ray crystallography;[22] the H⋯H distances are long (ca. 1.7 Å) and show that this is a classical hydride structure. The apparent disparity in the measured Re–H(B) distances (1.53 (7) and 2.06 (7) Å), while greater than 3σ, is not considered to be significant in view of the difficulty of determining H atom positions in the presence of heavy metals by X-ray diffraction.[23] Whatever the details of the Re–H–Re bonding, this complex is electronically unsaturated to an extent unusual for the heavier transition elements. It can be expected to be very reactive, although it has the remarkable property of being stable in air and water.[24] We find that it reacts with CO in 1-propanol to afford the carbonyl complex $[Re_2(\mu\text{-}H)(\mu\text{-}dmpm)_3(CO)_4]PF_6$ in which each Re atom has two terminal CO ligands bound to it and the structure of the $[Re_2(\mu\text{-}H)(\mu\text{-}dmpm)_3]$ unit of the parent cation is retained.[25] Studies on the reactivity of $[Re_2H_5(dmpm)_3]PF_6$ are being undertaken, and full details will be reported in due course.

Acknowledgment. Support from the National Science Foundation, through Grant No. CHE88-07444 to R.A.W. and Grant No. CHE86-15556 for the purchase of the microVAX II computer and diffractometer, is gratefully acknowledged. We also acknowledge the National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 8714258) for funds for the purchase of the NMR spectrometers.

Supplementary Material Available: A listing of atomic positional parameters for the structure of $[Re_2H_5(dmpm)_3]PF_6$ and a figure (Figure S1) showing some of the NMR spectral properties of this complex (5 pages). Ordering information is given on any current masthead page.

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[19] Yellow crystals of $[Re_2H_5(dmpm)_3]PF_6$ are monoclinic, space group $P2_1/n$, with $a = 9.288$ (1) Å, $b = 24.515$ (3) Å, $c = 13.761$ (3) Å, $\beta = 93.23$ (1)°, $V = 3128$ (1) Å^3, $Z = 4$, and $d_{calcd} = 1.976$ g/cm^3. X-ray data were collected at −100 °C on a 0.36 × 0.15 × 0.13 mm crystal for 5499 independent reflections having $4° < 2\theta < 50°$ on an Enraf-Nonius diffractometer using graphite-crystal-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Lorentz and polarization corrections were applied to the data. The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were identified in succeeding difference Fourier syntheses. The five hydride ligands were located following anisotropic refinement of all non-hydrogen atoms. Hydrogen atoms of the dmpm ligands were included at fixed positions. An empirical absorption correction was applied,[20] but no correction for extinction was made. The non-hydrogen atoms of the dirhenium complex and the atoms of the PF_6^- anion were refined anisotropically; corrections for anomalous scattering were applied to these atoms.[21] The final residuals were $R = 0.030$ ($R_w = 0.039$) for 4476 data with $I > 3\sigma(I)$.

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[23] Interestingly, if such a difference was real it could be considered as evidence for a structure in which the two Re atoms had different electron counts, i.e., 14-electron and 16-electron. In this event, the species would show some resemblance to the unsymmetrical complex $(Me_2NH)(CO)_4Re(\mu\text{-}H)Re(CO)_4Cl$, which is formally composed of 18-electron and 16-electron fragments: Adams, R. D.; Kuhns, J. D. *Polyhedron* **1988**, *7*, 2543.

[24] A solution of $[Re_2H_5(dmpm)_3]^+$ in D_2O shows a Re*H* resonance as a binomial septet at δ −9.0 (J_{HP} = 8.7 Hz).

[25] This has been confirmed by a single-crystal X-ray structure analysis which shows the Re–Re distance to be 3.3625 (4) Å: Fanwick, P. E., unpublished results.

Formation and Characterization of an 84-Electron Hexaruthenium Cluster: Spontaneous Decarbonylation of $H_2Ru_6(CO)_{18}$ To Form $H_2Ru_6(CO)_{17}$

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Reported herein are the preparation and characterization of $H_2Ru_6(CO)_{17}$, a cluster that contains an equal number of vertices and skeletal electron pairs.[1] It is formed through the loss of CO from $H_2Ru_6(CO)_{18}$ (eq 1).

$$H_2Ru_6(CO)_{18} \xrightarrow{\text{room temperature}} H_2Ru_6(CO)_{17} + CO \qquad (1)$$

Although $H_2Ru_6(CO)_{18}$ was first reported some 20 years ago and has been studied in several laboratories,[2-6] its spontaneous decarbonylation at room temperature is a previously unrecognized

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