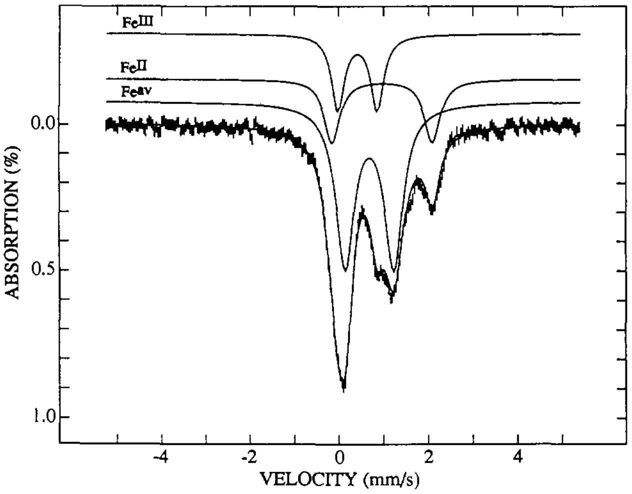

Figure 2. Mössbauer spectrum of polycrystalline $(Et_4N)[Fe_2(salmp)_2]$ at 297 K. The solid line through the data is the result of a least-squares fit to three doublets using the parameters in Table I. Curves shown above the data outline the individual quadrupole doublets.

Table I. Mössbauer Spectroscopic Parameters of Polycrystalline $(Et_4N)[Fe_2(salmp)_2]$ at 297 K

site	ΔE_Q, mm/s	δ, mm/s	Γ_l,[a] mm/s	Γ_h,[a] mm/s	%[b]
Fe^{II}	2.24	0.99	0.44	0.39	20
Fe^{III}	0.88	0.44	0.35	0.35	20
Fe^{av}	1.08	0.71	0.44	0.55	60

[a] Full width of low- and high-energy doublet lines. [b] Percent of total absorption. Because the recoilless fractions of the three components may differ at 297 K, the percentages do not necessarily correspond to the fraction[5] of molecules in the designated states.

is typical for octahedral Fe(III) sites with O/N coordination.[11] (iii) The z-axes of both electric field gradient tensors are tilted by $\beta \cong 30°$ relative to the z-axis of the common zero-field splitting tensor.

At 100 K the electronic relaxation is fast, and the Mössbauer spectrum consists of two doublets characteristic of localized Fe(III) and Fe(II) sites. At somewhat higher temperatures, a new doublet (Fe^{av}) appears; its intensity increases gradually as the temperature is raised. The spectrum of polycrystalline **2** in Figure 2 has been analyzed as follows. The high-energy features of all three doublets are well resolved. Assuming that the temperature dependencies of the δ values of the Fe^{II} and Fe^{III} sites are determined solely by the second-order Doppler shift ($\delta_{4.2K} - \delta_{300K} = 0.12$ mm/s), the two positions of the low-energy lines in the unresolved feature at ca. 0 mm/s can be fixed. With this information, the position of the low-energy line of the Fe^{av} doublet can then be calculated. For the final least-squares fit, the Fe^{II} and Fe^{III} doublets were constrained to have the same absorption area. The Mössbauer parameters listed in Table I convey an unusual result, viz., that the isomer shift of the Fe^{av} doublet is exactly the average of the shifts of the Fe^{III} and Fe^{II} sites.

From the preceding results, we draw the following conclusions concerning the electronic structure of mixed-valence **2**. (1) The complex is ferromagnetically coupled to afford an $S = 9/2$ ground state, which is well isolated from other states of the spin ladder. (2) Below 100 K, the complex is valence-trapped (class II[12]) in the polycrystalline state and in acetonitrile and DMA solutions. (3) Above 100 K, the complex exists as an apparent equilibrium mixture of valence-trapped (ca. 40% at 297 K) and "valence-detrapped" forms. Collective properties 1–3 are unique to this subset of oxygen-bridged iron dimers. All other synthetic iron dimers with various oxygen bridge modes,[1] including those in the $Fe_2(\mu\text{-}OR)_2$ set, are antiferromagnetically coupled, as are binuclear units in proteins.[3,13] The oxygen-bridged dimers $[Fe_2(hxta)(OAc)_2]^{2-}$ [9] and $[Fe_2(bpmp)(EtCO_2)_2]^{2+}$,[10] with the bridges $Fe_2(\mu\text{-}OR)(\mu\text{-}\eta_2\text{-}RCO_2)_2$, are valence-trapped (at least up to $T \approx 55$ K) but are antiferromagnetic. $[Fe_2(Me_3tacn)_2(OH)_3]^{2+}$ has an $S = 9/2$ ground state but is valence-delocalized (an example of double exchange[14]) very possibly because, unlike **2** (Fe–Fe = 2.79, 2.83 Å[1]), it is triply bridged with a short Fe–Fe distance (2.50 Å).[15] No other binuclear Fe complex displays property (3). Additional experiments are aimed at determining whether the doublet Fe^{av} reflects valence-detrapping (transitions between Fe^{III} and Fe^{II} that are fast on the Mössbauer time scale but slow on the vibrational time scale) or actual valence delocalization.[16] The results summarized here and elsewhere[1,3] emphasize the diversity of electronic properties of oxygen-bridged Fe complexes and the dependency of these properties on the details of the bridging interactions. Ferromagnetic binuclear Fe units now are a possibility that must be considered in analyzing the electronic structures of proteins.[13,17]

Acknowledgment. This research was supported at the University of Minnesota by NSF Grant DMB 86-05050 and at Harvard University by NIH Grant GM 28856.

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(10) Borovik, A. S.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2345.

(11) This comparison cannot be made for the Fe(II) site because its **a**-tensor is expected to be quite anisotropic. Owing to the uniaxial nature of the ground Kramers doublet, only the components of the magnetic hyperfine tensor along the y-axis are determined at 1.5 K. We can, however, assume that $\mathbf{a}_x \approx \mathbf{a}_y \approx \mathbf{a}_z$ for high-spin Fe(III). The observed magnetic hyperfine tensors **A** of the coupled $S = 9/2$ state are related to the intrinsic **a**-tensors of each site by $\mathbf{A}(Fe^{II}) = (4/9)\mathbf{a}(Fe^{II})$ and $\mathbf{A}(Fe^{III}) = (5/9)\mathbf{a}(Fe^{III})$.

(12) Robin, M. D.; Day, P. *Adv. Inorg. Radiochem.* **1967**, *10*, 247.

(13) Apparent exceptions are several ligated forms of deoxyhemerthyrin which are ferromagnetic, but the nature of the bridge between the two Fe(II) sites is unknown: Reem, R. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 1216.

(14) Münck, E.; Papaefthymiou, V.; Surerus, K. K.; Girerd, J.-J. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1988; Chapter 15.

(15) Drüeke, S.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Ding, X.-Q.; Bill, E.; Sawaryn, A.; Trautwein, A. X.; Winkler, J.; Gurman, S. J. *J. Chem. Soc., Chem. Commun.* **1989**, 59.

(16) At 1.5 K and 100 K the Mössbauer spectra of **2** as a polycrystalline sample and in DMA solution are essentially the same. Poor signal-to-noise in DMA (mp −20 °C) at 210 K did not allow us to resolve the question whether the appearance of Fe^{av} is a solid-state effect or an intrinsic electronic phenomenon; samples enriched in ^{57}Fe are in preparation.

(17) Note that the electronically delocalized $Fe_2(\mu\text{-}S)_2$ substructure of a protein Fe_3S_4 cluster has $S = 9/2$: Papaefthymiou, V.; Girerd, J. J.; Moura, I.; Moura, J. J. G.; Münck, E. *J. Am. Chem. Soc.* **1987**, *109*, 4703.

Reductive Elimination of Methane from a Cationic Rhenium Methyl Hydride. Evidence for an Intermediate Methane Complex

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Although intramolecular "agostic" interactions between transition-metal centers and pendant C–H bonds are well-characterized,[1] there is less evidence for the coordination of free hydrocarbon C–H bonds to transition-metal moieties.[2] Such σ complexes of alkanes are of great importance due to the intense current interest in homogeneous alkane activation reactions.[3] As part of our studies of the reactivity of rhenium alkyls of the type

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(1) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408. Brookhart, M.; Green, M. L. H.; Wang, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124.

(2) Although transition-metal alkane complexes have not yet been completely characterized, there is substantial spectroscopic data in support of such interactions, cf.: (a) Church, S. P.; Grevels, F. W.; Hermann, H.; Schaffner, K. *Inorg. Chem.* **1985**, *24*, 418–422. (b) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791–4808. (c) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276–2285.

(3) Bergman, R. G. *Science* **1984**, *223*, 902–908. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. Graham, W. A. G. *J. Organomet. Chem.* **1986**, *300*, 81–91.

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$(\eta\text{-}C_5H_5)_2Re\text{-}R$,[4] we have found that protonation of $(\eta\text{-}C_5H_5)_2Re\text{-}CH_3$ affords an isolable Re(V) methyl hydride $[(\eta\text{-}C_5H_5)_2Re(H)CH_3]X$[5] ($X = Cl^-$, **1**; $X = BF_4^-$, **2**), which undergoes alkyl/hydride site exchange much more rapidly than reductive elimination of methane. Similar site exchange reactions have been reported by Norton and co-workers in a study of $(\eta\text{-}C_5H_5)_2W(CH_3)H$[6] and by Bergman and Periana[7] in the case of (η-(hapto-)$C_5Me_5)Rh(PMe_3)(R)H$ (R = various alkyl groups).

Reductive elimination of CH_4 from **1** was studied in the temperature range 253–293 K in CD_2Cl_2 solutions.[8] The temperature range employed was limited due to the extreme sensitivity of the rate of elimination to temperature. Consistent with these observations, an Eyring plot of the data gives $\Delta H^{\ddagger} = 28.1 \pm 1.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 27 \pm 6$ cal mol^{-1} deg^{-1}. The entropy of activation is exceptionally large and positive in comparison to other reported data for alkyl hydride reductive eliminations.[10] In order to further define the mechanism of methane formation, reductive elimination of methane from **1** was also studied in methanol and acetonitrile. The rate of reductive elimination was affected only slightly by these changes in the reaction solvent.[11] The presence of PPh_3 (1 equiv) did not affect the rate of reductive elimination. Reductive elimination of methane from **1** and **1**-d_4 was examined at 282 K. An *inverse* kinetic isotope effect ($k_H/k_D = 0.8$ (1)) was observed. The reductive elimination of methane is not reversible. When **1**-d_4 was allowed to undergo partial reductive elimination under CH_4 (ca. 30 psi), no proton incorporation into **1** was observed.

In order to establish the molecularity of this reductive elimination reaction, methane elimination from **2**-d_3 was also studied. Only methane-d_3 was formed.[12] Thus bimolecular pathways for this reaction can be discounted. In the course of these investigations, site exchange between the methyl and hydride positions was noted. The equilibrium of eq 1 was established rapidly at 243 K. The equilibrium constant $K_{eq} = 1.0 \pm 0.1$ for eq 1. This

$$[(\eta\text{-}C_5H_5)_2Re(H)CD_3]^+ \rightleftharpoons [(\eta\text{-}C_5H_5)_2Re(D)(CHD_2)]^+ \qquad (1)$$

is substantially less than the statistical value of 3.[13] Thus the equilibrium isotope effect leads to a substantial preference for deuterium in the methyl site. The rate of approach to equilibrium was monitored at 210–243 K. As in the case of reductive elimination, the rate of the exchange reaction is very sensitive to temperature. An Eyring plot of the data gives $\Delta H^{\ddagger} = 22.3 \pm 1.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = 24 \pm 9$ cal mol^{-1} deg^{-1}. Since site exchange occurs much more rapidly than reductive elimination, the observation that only CD_3H is formed from **2**-d_3 establishes that *both* site exchange and reductive elimination are *intramolecular* processes. Site exchange reactions similar to the one occurring in this rhenium system have been described previously,[6,7,10a] but this is the first example where the rate of site exchange and the rate of reductive elimination are sufficiently different that the two processes can be separately investigated.

There is a striking similarity in the entropy of activation for the site exchange and the reductive elimination reaction. Since we are dealing with a cationic complex, the role of solvation in determining the entropy differences between the ground-state methyl hydride and the transition states for site exchange and reductive elimination could be quite important. As noted above, reductive elimination from **1** occurs approximately four times faster in methanol than in dichloromethane. This reaction was also studied as a function of temperature in the range 255–285 K, giving $\Delta H^{\ddagger} = 28.2 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = 29 \pm 4$ cal mol^{-1} deg^{-1}. Since the entropy of activation does not differ significantly (within experimental error) in these two solvents, it seems unlikely that solvation effects are major contributors to the large, positive entropy of activation.

The observation of an inverse kinetic isotope effect for reductive elimination is consistent with the operation of a rapid preequilibrium of the ground-state methyl hydride with an intermediate on the reaction coordinate for reductive elimination.[15] The observed effect is explicable if the intermediate is formed in greater concentration for the deuterated species than for the protio species. This is a reasonable expectation, since formation of the intermediate requires scission of a Re–H(D) bond and formation of a stronger C–H(D) bond. Similar inverse kinetic isotope effects have now been observed in alkane reductive elimination from several alkyl hydride complexes.[7,10a] In contrast, there are several examples of reductive elimination reactions with normal (positive) kinetic isotope effects.[16]

The observations outlined above provide ample evidence that an intermediate exists on the reaction coordinate for reductive elimination of methane from **1** and **2**. We postulate that the intermediate for reductive elimination is also involved in the more rapid site exchange reaction and that this intermediate is a methane σ complex. At this point, the structure of the intermediate remains obscure, but it is interesting to consider how the site exchange process might occur. An intuitively appealing possibility is a species with *two* C–H(D) bonds coordinated to the metal center.[17] Exchange of coordinated for free C–H bonds

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(4) (a) Stucky, G. D.; Mink, R. I.; Welter, J. J.; Young, P. R. *J. Am. Chem. Soc.* **1979**, *101*, 6928–6933. (b) Ephritikine, M.; Baudry, D. *J. Organomet. Chem.* **1980**, *195*, 213–222.

(5) Complexes **1** and **2** have been isolated as colorless microcrystalline precipitates by low-temperature precipitation from Et_2O: ^1H NMR (CD_2Cl_2, 273 K, δ (ppm), intensity and assignment) **1**, 5.69, 10 H, (η-C_5H_5), 0.60, 3 H, CH_3, −12.22, 1 H, hydride; **2**, 5.46, 10 H, (η-C_5H_5), 0.60, 3 H, CH_3, −12.11, 1 H, hydride.

(6) Bullock, R. M.; Headford, C. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727–729.

(7) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332–7346.

(8) The product of methane elimination from **1** is $(\eta\text{-}C_5H_5)_2Re\text{-}Cl$, which was conclusively identified by comparison to an authentic sample.[4b] Progress of reaction was monitored by ^1H NMR integration, with appropriate pulse delays. Probe temperatures were obtained by calibration against the chemical shifts of methanol. Fluctuations in probe temperature over the course of the experiments were typically ±0.2 °C. Reproducibility of rate constants is approximately ±15%, as shown by the results of duplicate determinations at the same temperature. Uncertainties in the activation parameters were evaluated by using the procedure of Markgraf and co-workers.[9]

(9) Peterson, R. C.; Markgraf, J. H.; Ross, S. D. *J. Am. Chem. Soc.* **1961**, *83*, 3819–3823.

(10) Reported values of $\Delta S^{\ddagger}$ for alkane reductive elimination reactions cover a wide range. Some representative examples are as follows: (a) $(\eta\text{-}C_5Me_5)Ir(PMe_3)(cyclohexyl)H$, $\Delta S^{\ddagger} = 10$ (2) cal mol^{-1} deg^{-1}. Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550. (b) $(\eta\text{-}C_5H_5)_2W(CH_3)H$, $\Delta S^{\ddagger} = -4$ (1) cal mol^{-1} deg^{-1} (ref. 6). (c) *cis*-$(PPh_3)_2PtH(CH_2CF_3)$, $\Delta S^{\ddagger} = 5(2)$ cal mol^{-1} deg^{-1} (benzene). Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831–1834. (d) *cis*-$(Cy_2PCH_2CH_2PCy_2)PtH(CH_2CMe_3)$, $\Delta S^{\ddagger} = 5$ (1) cal mol^{-1} deg^{-1}. Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436–1448. (e) Thermolysis of $(Et_3P)_2Pt(CH_2CH_3)_2$ in the presence of PEt_3 gives ethane, PEt_3, and $(PEt_3)Pt(C_2H_4)$ via rate-determining reductive elimination from an intermediate alkyl hydride. $\Delta S^{\ddagger} = 35$ (5) cal mol^{-1} deg^{-1}. In this case, the activation entropy is probably a composite of contributions from the reductive elimination and the PEt_3 loss/β elimination which occur prior to reductive elimination. (f) The rate of reductive elimination of methane from $(\eta\text{-}C_5Me_5)Rh(PMe_3)H(CH_3)$ is reported to accelerate very rapidly with increasing temperature, which prevented the measurement of activation parameters. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650–1663. This observation is consistent with a large positive $\Delta S^{\ddagger}$.

(11) Rate constants (280 K) for reductive elimination from **1** in CD_2Cl_2, CD_3CN, and CD_3OD are 3.1×10^{-4}, 6.0×10^{-4}, and 12.3×10^{-4} s^{-1}, respectively. In a comparison of **1** and **2**, reductive elimination was monitored at 282 K in dichloromethane. Rate constants are 5.5×10^{-4} and 7.6×10^{-4} s^{-1}, respectively.

(12) The isotopomers of methane were assayed by ^1H NMR (500 MHz). The various isotopomers were clearly resolved. Methane-d_3 accounts for >95% of the methane evolved (see Supplementary Material).

(13) A similar equilibrium isotope effect ($K_{eq} = 1.4$) has been reported for $(\eta\text{-}C_5H_5)_2W(H)CD_3$ by Norton and co-workers.[6] Other examples of such equilibrium isotope effects are reported in footnote 15 of ref 6.

(14) $(\eta\text{-}C_5Me_5)Rh(PMe_3)H(Me)$: Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814–4819.

(15) It is unlikely that this inverse kinetic isotope effect has a significant contribution from *secondary* isotope effects, since the carbon remains sp^3 hybridized throughout. Due to the rapid site exchange process, it is impossible to experimentally evaluate the contribution from secondary effects. Explanations of inverse kinetic isotope efects have been discussed. cf.: Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley Interscience: New York, 1980; p 157. It is unlikely that an inverse isotope effect can result from a single elementary step. When an inverse isotope effect is observed, this implies that an intermediate exists which is in equilibrium with the ground state. A discussion of this problem with respect to reductive elimination reactions is found in ref 7.

(16) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332–338.

could occur via dissociation of one of the coordinated bonds, followed by rotation of the now unconstrained methyl group, and subsequent recoordination of a new C-H(D) bond.

The rate difference between the site exchange reaction and the reductive elimination reaction appears to be almost entirely enthalpic in origin, amounting to ca. 6 kcal mol^{-1}. The transition states for these two reactions presumably differ in that the former contains bound methane, while in the latter the methane is essentially dissociated. Thus the enthalpy difference may approximate the binding energy of methane.[19] For comparison, calculated binding energies for methane in $Pd(CH_4)$ and $Pt(CH_4)$ are 2 and 5 kcal mol^{-1}, respectively.[17]

We are continuing to investigate the coordination chemistry of other alkanes to the rhenocene cation and derivatives in order to assess the steric and electronic factors which influence alkane binding.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Support for this investigation was also provided by the National Science Foundation (Grant CHE-8814191). The receipt of a Cottrel Grant from the Research Corporation is gratefully acknowledged. We thank Professors Jack Norton and John Bercaw for providing information prior to publication.

Supplementary Material Available: Kinetic data and Eyring plots for reductive elimination and site exchange reactions and proton NMR spectrum of methane-d_3 formed by reductive elimination from **2**-d_3 (6 pages). Ordering information is given on any current masthead page.

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(17) There is some theoretical support for this description of the intermediate provided by GVB calculations on the interaction of methane with Pd and Pt atoms. Low, J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609-622. Experimental evidence for species having two C-H bonds coordinated to a transition-metal center is provided by the studies of Fehlner and co-workers on $Fe_3(CO)_9(CH_4)$.[18]

(18) Fehlner, T. P.; Jacobsen, G. B.; Vites, J. C.; Dutta, T. K. *Organometallics* **1987**, *6*, 842-847.

(19) This enthalpy difference would actually represent the *minimum* binding energy for methane since it actually corresponds to the enthalpy differences between the two transition states (reductive elimination versus site exchange processes). The actual binding energy will be greater by an amount equal to the stabilization of the intermediate, which is not known.

Isolation, Structure, and Magnetic Properties of a Novel Mononuclear Rhodium(II) Complex

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The chemistry of divalent rhodium is confined almost exclusively to binuclear metal-metal bonded complexes,[1] with only sporadic reports of isolated Rh(II) monomers having appeared in the literature to date.[2,3] In many cases, the assignment of the +2 oxidation state is ambiguous; in fact, to our knowledge, only one paramagnetic mononuclear rhodium compound, the square-planar molecule $Rh(MNT)_2^{2-}$, has been structurally characterized.[2a] The paucity of mononuclear d^7 rhodium species as opposed to the abundance of cobalt(II) monomers may be understood in terms of the greater stability of the Rh-Rh single bond. A great deal of synthetic and theoretical work has been devoted to the understanding of the bonding in Rh_2^{4+} complexes.[1]

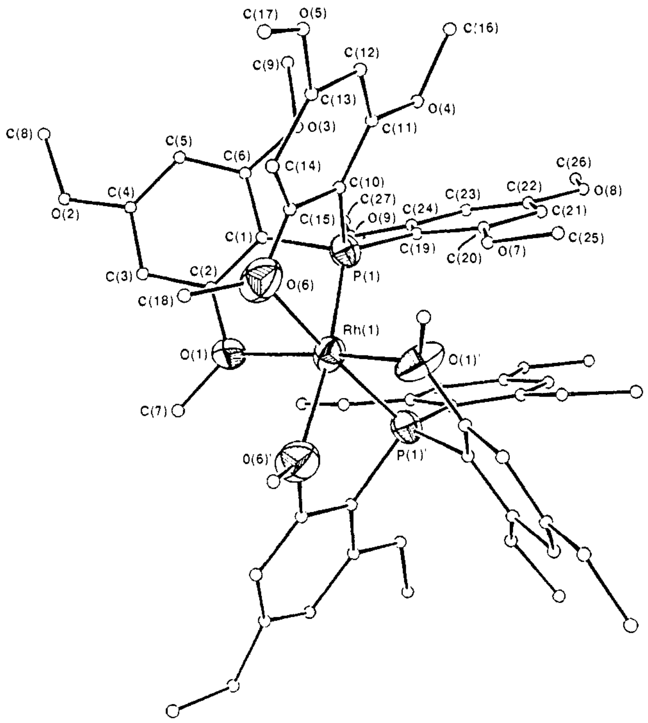

Figure 1. ORTEP representation of the $[Rh(TMPP)_2]^{2+}$ molecular cation. Some important distances (Å) and angles (deg) are as follows: Rh(1)-P(1), 2.216 (2); Rh(1)-O(1), 2.398 (5); Rh(1)-O(6), 2.201 (6); O(1)-C(2), 1.393 (9); P(1)-Rh(1)-P(1), 105.2 (1); P(1)-Rh(1)-O(1), 80.5 (1); P(1)-Rh(1)-O(6), 171.5 (2); O(1)-Rh(1)-O(1), 167.8 (3).

One of our current research interests is the coordination chemistry of solvated polynuclear metal cations, especially our recently reported rhodium(II,II) complex, $[Rh_2(CH_3CN)_{10}](BF_4)_4$.[4] Few entirely solvated binuclear transition-metal cations are known, the only other examples being $M_2(aq)^{4+}$ (M = Mo,[5] Rh[6]) and $[Mo_2(CH_3CN)_8]^{4+}$;[7] the chemistry of these remains virtually unexplored. In order to circumvent the problems associated with preparing and handling aqua species, we have developed a convenient synthesis for the CH_3CN derivative of Rh_2^{4+} (vide supra), a compound that allows easy access to unusual monomeric and polynuclear compounds of Rh(II). We now wish to report the synthesis of a pseudo-octahedral rhodium(II) monomer stabilized only by two bulky phosphine ligands. The ligand is TMPP (TMPP = tris(2,4,6-trimethoxyphenyl)phosphine) which has been recently synthesized and fully characterized.[8] We are engaged in a broad study of the coordination and organometallic

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(1) (a) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73 and references therein. (b) Boyar, E. B.; Robinson, S. D. *Coord. Chem. Rev.* **1983**, *50*, 109 and references therein.

(2) For mononuclear Rh(II) coordination complexes, see: (a) Billig, E.; Shupack, S. I.; Waters, J. H.; Williams, R.; Gray, H. B. *J. Am. Chem. Soc.* **1964**, *86*, 926. (b) Mezharaush, G. P. *Izv. Akad. Nauk. Latv. SSR. Ser. Khim.* **1965**, 263. (c) Pneumatikakis, G.; Psaroulis, P. *Inorg. Chim. Acta.* **1980**, *46*, 97. (d) Bennett, M. A.; Bramley, R.; Longstaff, P. A. *J. Chem. Soc., Chem. Commun.* **1966**, 806. (e) Bennett, M. A.; Longstaff, P. A. *J. Am. Chem. Soc.* **1969**, *91*, 6266. (f) Masters, C.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 3679. (g) Moers, F. G.; de Long, J. A. M.; Beaumont, P. M. H. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1915.

(3) For mononuclear organometallic Rh(II) complexes, see: (a) Fischer, E. O.; Lindner, H. H. *J. Organomet. Chem.* **1964**, *1*, 307. (b) Fischer, E. O.; Wawersik, H. *J. Organomet. Chem.* **1966**, *5*, 559. (c) Keller, H. J.; Wawersik, H. *J. Organomet. Chem.* **1967**, *8*, 185. (d) Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112. (e) Dessy, R. E.; Kornmann, R.; Smith, C.; Hayter, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001.

(4) (a) Dunbar, K. R. *J. Am. Chem. Soc.* **1988**, *110*, 8247. (b) Dunbar, K. R.; Pence, L. E., unpublished results.

(5) (a) Bowen, A. R.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287. (b) Bowen, A. R.; Taube, H. *Inorg. Chem.* **1974**, *13*, 2245.

(6) (a) Maspero, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 7361. (b) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 2276. (c) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 405. (d) Ziolkowski, J. J.; Taube, H. *Bull. Acad. Pol. Sci. Ser. Chim.* **1973**, *21*, 113.

(7) Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2274.

(8) (a) Wada, M.; Higashizaki, S. *J. Chem. Soc., Chem. Commun.* **1984**, 482. (b) Dunbar, K. R.; Haefner, S. C., manuscript in preparation.

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