

Figure 4. IR spectra of 1.5 mM solutions of $[\text{Rh}_2(\text{TM4})_4][\text{TFPB}]_2$ in 0.1 M TBA^+X^- in CH_2Cl_2 after the removal of 1 equiv of charge: (A) $\text{X} = \text{ClO}_4^-$; (B) $\text{X} = \text{PF}_6^-$; (C) $\text{X} = \text{TFPB}^-$.

response, due to the increased stability of $\text{Rh}_2(\text{TM4})_4^{4+}$ afforded by the coordination of ClO_4^- .

The lack of a second oxidation of $\text{Rh}_2(\text{TM4})_4^{3+}$ to $\text{Rh}_2(\text{TM4})_4^{4+}$ in $\text{TBA}^+\text{TFPB}^-$ precludes an accurate assessment of K_{disp}' ; however, on the basis of the difference between the $E^{\circ'}_{3+/2+}$ couple and the anodic limit, we can place an upper limit on the disproportionation of $\text{Rh}_2(\text{TM4})_4^{3+}$ of 1×10^{-10} . At 25 °C, this translates into a disproportionation reaction that is endothermic by greater than 13.5 kcal/mol. Table II summarizes the disproportionation constants of $\text{Rh}_2(\text{TM4})_4^{3+}$ in the presence of a variety of common electrolyte anions. The relative ability of these anions to stabilize the $\text{Rh}_2(\text{TM4})_4^{4+}$ core follows the order $\text{Cl}^- \gg \text{ClO}_4^- > \text{BF}_4^- > \text{PF}_6^- > \text{SbF}_6^- \gg \text{TFPB}^-$. This series closely follows a previous ordering of the relative nucleophilicities of several common anions based on quantum yield studies of the photosubstitution of $\text{CpFe}(\text{toluene})^+\text{X}^-$ CH_2Cl_2 solutions.³⁰

By making the assumption that the difference between $\Delta G_{\text{disp}}'$ in TBA^+X^- and $\Delta G_{\text{disp}}'$ in $\text{TBA}^+\text{TFPB}^-$ is due primarily to differences in the coordinating abilities of X^- and TFPB^- , it is possible to assess the relative thermodynamics of associating various anions with the $\text{Rh}_2(\text{TM4})_4^{4+}$ core. Our data demonstrate that TFPB^- interacts far less than the standard noninteracting anions.³¹ For example, we find that $\text{Rh}_2(\text{TM4})_4^{4+}$ is more than 12 kcal/mol more stable in the presence of PF_6^- than in the presence of TFPB^- . Figure 4 shows this pictorially by plotting the IR spectra of equimolar solutions of $\text{Rh}_2(\text{TM4})_4^{2+}$ after the removal of 1 equiv of charge in the presence of ClO_4^- , PF_6^- , and TFPB^- . While both the ClO_4^- solution (top curve) and PF_6^- solution (middle curve) show substantial amounts of $\text{Rh}_2(\text{TM4})_4^{4+}$, the TFPB^- solution

(bottom curve) consists only of $\text{Rh}_2(\text{TM4})_4^{3+}$.

Conclusions. We have found that $\text{TBA}^+\text{TFPB}^-$ is very useful as a noninteracting electrolyte for electrochemical studies that generate electrophilic species. Quantitative studies with an anion-sensitive redox couple indicate that a difference of greater than 22 kcal/mol is spanned by the series $\text{Cl}^- > \text{ClO}_4^- > \text{BF}_4^- > \text{PF}_6^- > \text{SbF}_6^- > \text{TFPB}^-$. Surprisingly, the TFPB^- ion is nearly 11 kcal/mol less interactive than SbF_6^- , which is generally regarded as a very poorly interactive anion. We believe that this interaction ordering will be generally applicable but might break down for species which show a particular propensity to abstract F^- from the fluoride-containing anions in the series.⁴ Future studies will further address the coordinating ability of the TFPB^- ion and other potentially less coordinating anions which we are currently studying.

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Registry No. $\text{TBA}^+\text{TFPB}^-$, 112724-99-9; CH_2Cl_2 , 75-09-2; Cp_2Ru , 1287-13-4; Cp_2Os , 1273-81-0; $\text{Rh}_2(\text{TM4})_4^{2+}$, 73367-41-6; Cp_2Ru^+ , 54538-51-1; Cp_2Os^+ , 54438-61-8; Cp_2Fe , 102-54-5; Cp_2Fe^+ , 12125-80-3; TBA^+Cl^- , 1112-67-0; $\text{TBA}^+\text{ClO}_4^-$, 1923-70-2; $\text{TBA}^+\text{BF}_4^-$, 429-42-5; $\text{TBA}^+\text{PF}_6^-$, 3109-63-5; $\text{TBA}^+\text{SbF}_6^-$, 22505-58-4; $\text{Rh}_2(\text{TM4})_4^{3+}$, 137039-42-0; $[\text{Rh}_2(\text{TM4})_4][\text{TFPB}]_2$, 137039-43-1; $[\text{Rh}_2(\text{TM4})_4][\text{Cl}]_2$, 99327-01-2.

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Pd-H-P Bridging in a Palladium(I) Dimer

The ability of a carbon-hydrogen bond to function as a donor to a transition metal is now widely recognized.¹ Indeed, for the general case $\text{L}_n\text{M-H-E}$, with E = an appropriately substituted carbon, there is a continuum of bonding modes stretching from very weak to bridging.² In a more general vein, if one views an agostic interaction as one form of the class $\text{L}_n\text{M-H-E}$, where, apart from a carbon fragment, E can be a different transition metal³ or a nitrogen^{4,5} or boron⁶ function, then it is interesting to note that no representative with E = P is known, although this possibility has been recently mentioned.⁷

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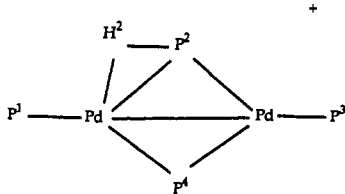
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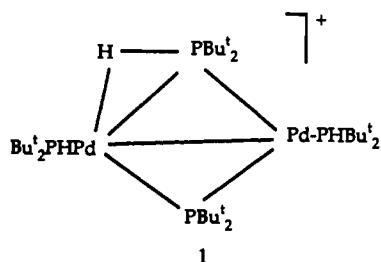
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Table I. NMR Parameters^a for Complex 1


	P ¹	P ²	P ³	P ⁴	H ¹	H ²	H ³
P ¹	47.7^b	96	65	21	322		
P ²	96	217.2	15	190	7.2	151	13
P ³	65	15	52.0^b	49			324
P ⁴	21	190	49	455.3	3.6	35	13
H ¹	322	7.2		3.6	4.92		
H ²		151		35		-0.16	
H ³		13	324	13			5.16

^a CD₂Cl₂, room temperature, 5.7 T. H¹ and H³ are bound to the corresponding ³¹P; CF₃SO₃⁻ salt. Chemical shifts (bold typeface) are in ppm; coupling constants (normal type) are in Hz. ^b P¹, H¹ and P³, H³ are correlated pairwise but not assigned individually; i.e., assignments can be reversed.

We report here the synthesis and characterization of the novel cationic complex **1** as its CF₃SO₃⁻ salt, which contains a Pd-H-P unit as shown by 1- and 2-dimensional NMR spectroscopy.



Cationic complex **1** was prepared via protonation of the corresponding neutral Pd(I) dimer, [Pd(PBu₂)(PHBu₂)]₂ (**2**),⁸ and is a violet colored solid. The crystal structure,⁹ determined by X-ray diffraction methods, reveals that the non-hydrogen atoms in **1** possess a center of symmetry, so that only half of the molecule

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- (8) Complex **1** was prepared by refluxing **2** (485 mg, 6.1 mmol) with 2 equiv of CF₃SO₃H in dimethoxyethane for 2 h. The product (462 mg, 80%) precipitates upon addition of diethyl ether. Complex **2** was prepared from the reaction of Pd(η³-C₃H₅)(cp) with PHPBu₂.
- (9) Crystal data for **1** (C₃₃H₇₅F₃O₃P₄Pd₂S): *M*_r = 945.76, space group *P*1̄ (No. 2); *a* = 10.245 (1), *b* = 10.739 (1), *c* = 22.624 (3) Å; α = 79.816 (9)°, β = 87.876 (10)°, γ = 68.266 (8)°; *V* = 2274.7 (5) Å³; *Z* = 2, ρ = 1.380 g cm⁻³; Mo Kα (graphite-monochromated λ = 0.710 69 Å); μ = 10.02 cm⁻¹. A prismatic crystal of approximate dimensions 0.2 × 0.2 × 0.1 mm was used for the data collection (room temperature) on a Nonius CAD 4 diffractometer using an ω/2θ scan and variable scan speed to ensure approximately constant statistical precision of the recorded intensities. A total of 6284 unique reflections (±*h*, ±*k*, +*l*) were collected (2θ_{max} = 46.0°) of which 4395 were considered as observed [*F*_o² > 4.0σ(*F*_o²)]. Data were corrected for absorption and decay; solution was by Patterson and Fourier methods with full-matrix least-squares refinement. The contribution of the hydrogen atoms in their calculated positions, C-H = 0.95 Å, P-H = 1.90 Å, and *B*_{iso}(H) = 1.5*B*(P,C), was taken into account but not refined. *R* = 0.054, *R*_w = 0.080, and GOF = 2.295 (375 refined parameters). There are (in space group *P*1̄) two independent half-molecules in the unit cell. An attempt to refine **1** in space group *P*1 led to significantly worse agreement factors and a greater spread of the bond lengths and angles. Moreover, this refinement failed to show the expected asymmetric coordination about the Pd atoms; i.e., both molecules are pseudosymmetric retaining an approximate center of symmetry between the Pd atoms. Therefore, the centrosymmetric model was retained. There are no significant differences (>2.0σ) in bond lengths and angles in the two independent "halves". The CF₃SO₃⁻ anion is disordered, as can be judged from the values of the thermal parameters. The primed atoms are related to the unprimed via the center of symmetry. All calculations were carried out using the SDP crystallographic package.

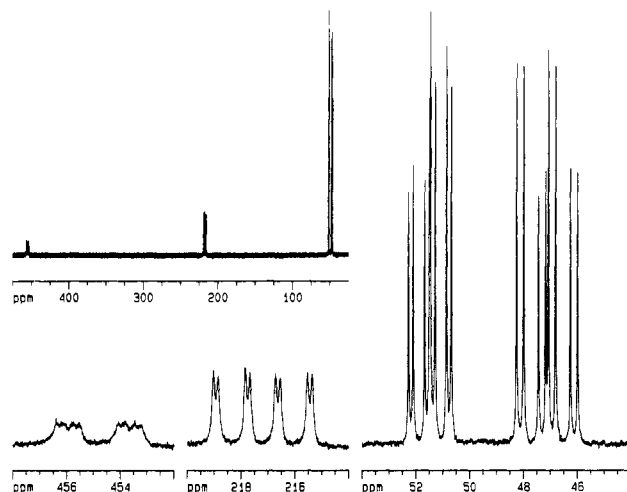


Figure 1. Phosphorus-31 NMR spectrum for **1**, showing the four non-equivalent phosphorus resonances (CD₂Cl₂, 101 MHz, Bruker AC-250).

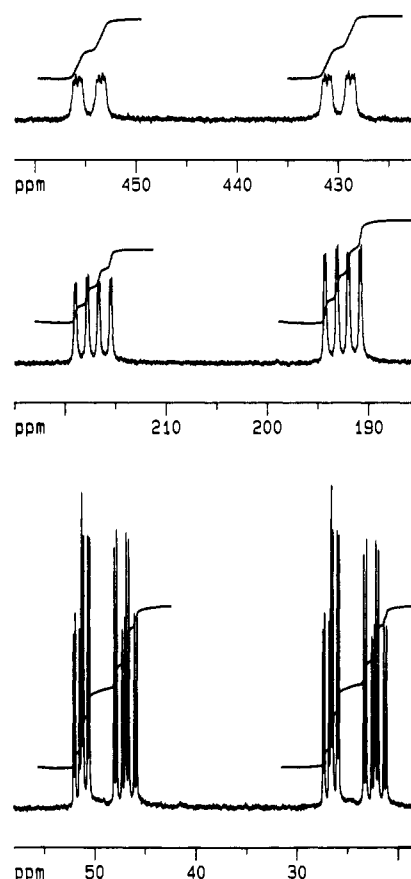


Figure 2. Heteronuclear Overhauser experiment showing enhancement of the phosphorus signal at 217.2 ppm upon irradiation of the hydride at -0.16 ppm. Each of the three traces shows one ³¹P resonance: left, unperturbed at its correct chemical shift; right, under the influence of irradiation (saturation). The integrals shown on each of the traces are a direct measure of the NOE for that ³¹P spin (Bruker AC-200).

is independent.¹⁰ There are two different phosphorus ligands, one of which is bridging. The terminal Pd-P separation is 2.327 (2) Å and is normal¹¹ whereas the two Pd-P distances involving

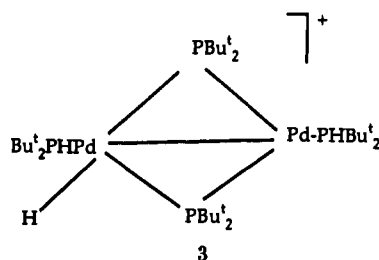
- (10) The presence of a crystallographic center of symmetry implies that the coordination sphere at each Pd atom must be identical. This is in contradiction to the solution data, i.e. the presence of a single hydride atom, as opposed to two hydride atoms. Thus, the solid-state result can be explained as resulting from an average disordered situation obtained by superimposing two molecules having the structure **1** across the symmetry center. Preliminary ³¹P solid-state results suggest that the structure does not have a center of symmetry.

the bridging phosphides are 2.311 (2) and 2.393 (3) Å, with the latter rather long. The Pd–Pd bond length is 2.611 (1) Å. The hydride ligand was not found; however, we note⁹ that the P1–Pd–P2' angle of 134 (1)° is larger than the P1–Pd–P2 angle of 113 (1)°.

The phosphorus NMR spectrum reveals *four* nonequivalent groups of resonances, two of which are relatively low field and can be assigned to bridging phosphide ligands¹² (see Table I and Figure 1) as well as two with positions considered normal for coordinated palladium phosphines.^{13a} It is interesting to note that the two phosphide resonances are ca. 200 ppm apart, suggesting very different electronic environments for these ligands. This lower symmetry precludes a solution structure with a bridging hydride in a symmetrical position between the two bridging phosphides and, consequently, is in contradiction with the solid-state result.¹⁰

The proton spectrum for **1** reveals two different P–H protons from the secondary phosphines at 4.91 and 5.16 ppm, with normal^{13c} one-bond phosphorus–proton coupling constants of 322 and 324 Hz, respectively. The hydride ligand appears at ca. –0.16 ppm as a doublet of doublets with one large (151 Hz) and one smaller (35 Hz) coupling to the two *bridging* phosphorus spins. A summary of the relevant NMR data is presented in Table I.

At this point one might envision a solution structure such as **3**; this would result from the expectation that a 151-Hz coupling



should arise from a *trans* orientation of the two spins.¹⁴ One can show that this is *not* the source of this spin–spin interaction by 2-D ³¹P, ¹H NOE, and shift measurements. The hydride couples to the low-field phosphorus resonances, and the signal at 217.2 ppm is responsible for the 151-Hz value. Subsequent *heteronuclear* P, H Overhauser enhancement studies, done in both one-

and two-dimensional modes, clearly show a ca. 20–30% enhancement of the 217.2 ppm phosphorus signal upon hydride irradiation (1-D mode; see Figure 2) and strong crosspeaks from the hydride to this same phosphorus signal (2-D mode). Therefore, these spins are relatively close in space.

Preliminary calculations based on these Overhauser results suggest the P–H separation to be ca. 1.9 Å; consequently it is not possible for these spins to be *trans* to one another. It is reasonable, however, to place the hydride between the Pd and the bridging phosphide. This would be consistent with (1) the longish Pd–P separation of ca. 2.39 Å, (2) the wider angle of 134°, (3) the *reduced* one-bond coupling from its ca. 323 Hz value to 151 Hz,¹⁵ (4) the very different phosphorus chemical shifts, and (5) the proximity of P to H and consequently the observed NOE's.

It is worth remembering that protonation of bridging phosphide complexes has been reported¹⁶ and, in one case, leads to terminal hydride complexes so that our observed unusual bonding mode is most likely associated with the chemistry of Pd(I). A complete description of **1** and the starting material [Pd(PBu₂)(PHBu₂)]₂, as well as related derivatives, will appear shortly.

In conclusion we have shown that a new hydride bridging mode containing the Pd–H–P fragment is both feasible and isolable. We expect heteronuclear NOE experiments to be of increasing utility in the placement of H atoms within a coordination sphere.

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Registry No. **1**, 137091-85-1; **2**, 137091-86-2; Pd, 7440-05-3.

Supplementary Material Available: Tables S1–S6, listing crystallographic and experimental details, positional and thermal parameters, and bond angles and bond distances, an ORTEP view of **1** with the numbering scheme, and diagrams showing the numbering schemes for the two independent molecules (15 pages); Table S7, listing calculated and observed structure factors (44 pages). Ordering information is given on any current masthead page.

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