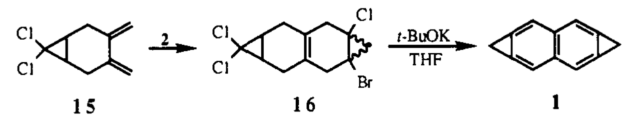
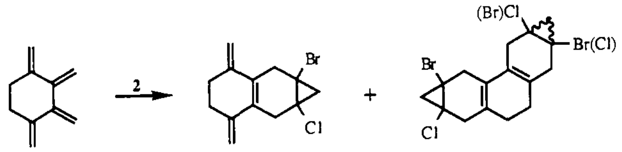
Scheme III



15 16 1

spectrum showed the characteristic benzene "double bond" at 1660 cm^{-1}. Elemental composition was provided by combustion analysis. Calcd for $C_{16}H_{10}$: C, 95.02; H, 4.98. Found: C, 94.95; H, 5.04.

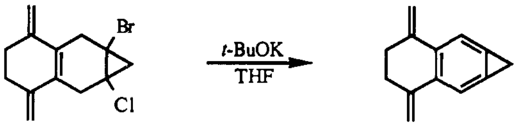
The starting material required for the synthesis of 1*H*,4*H*-dicyclopropa[*b*,*h*]phenanthrene (**4**) can be prepared from the reactive tetraene **8**.[12] Thus treatment of **8** with a 6-fold excess of **2** for 5 days at −20 °C gave adduct **9** (55% yield) along with the desired bis-adduct **10** (10% yield).



8 9 10

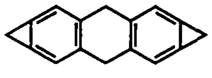
After separation by column chromatography, **10** was aromatized with DDQ in benzene at 65 °C for 18 h to yield **11** in 64% yield (Scheme II). Reaction of **11** with potassium *tert*-butoxide in THF provided **4**, mp 85–86 °C, in 84% yield after chromatography.

The interesting cyclopropa[*b*]naphthalene derivative **12** could be isolated in 57% yield when **9** was treated with potassium *tert*-butoxide. Surprisingly, the *tert*-butoxide/THF medium used to effect the elimination of **9** does not induce a base-catalyzed prototropic rearrangement of the double bonds in **12**.

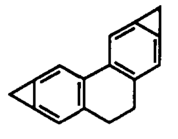


9 12

Treatment of **6** and **10** with potassium *tert*-butoxide in THF provided the dihydro derivatives **13** and **14** in 31% and 77% yields, respectively.[13]



13



14

Finally, this route can also be used as an alternative synthesis of **1** (Scheme III). Reaction of **2** with Garratt's diene (**15**)[7] yielded the cycloadduct **16** (42% yield), which could be converted readily into **1** (52% yield).

We are currently pursuing the preparation of other di- and tricyclopropenes. Results of these studies will be reported later.

Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation for support of this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We thank Scott Flanagan for the elemental analyses.

Supplementary Material Available: Experimental procedures for the syntheses of **1–14** and **16** including complete spectral characterization (3 pages). Ordering information is given on any current masthead page.

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(12) Hopf, H.; Gottschild, D.; Lenk, W. *Isr. J. Chem.* **1985**, *26*, 79. To the best of our knowledge, **8** has not been used previously in synthesis.

(13) These dicycloproparenes as well as **3** and **4** are surprisingly stable compounds, decomposing only slowly at −20 °C after several weeks.

Binuclear Palladium Complexes with Bridging Hydrides. Unusual Coordination Behavior of $LiBEt_4$

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Metal hydrides constitute an important class of molecules that have relevance to catalysis, organic synthesis, and hydrogen storage.[1] Although soluble metal hydride complexes are known for most of the transition elements, palladium derivatives containing hydride ligands are relatively rare.[2] This is particularly surprising since homogeneous catalysis by palladium complexes is well-known and in many cases participation by a palladium hydride[3] species is inferred. A number of square-planar derivatives of the formula *trans*-$PdH(X)(PR_3)_2$ have been prepared and characterized;[4] however, no examples of palladium dimers having bridging hydrides have been as yet unequivocally characterized.[5]

Our interest in the reactivity of binuclear hydride-bridged complexes[6] was incentive enough to examine the preparation of the noticeably absent palladium analogues of certain nickel and platinum dimers[7] of the formula $[P_2M]_2(\mu\text{-}H)_2$ where M = Ni or Pt and P_2 is bidentate phosphine. In this report the preparation of the first structurally characterized hydride-bridged dimer of palladium is described. An unexpected bonus in this work was the discovery that the dimer also has a $LiBEt_4$ molecule as part of the structure.

Addition of 2 equiv of a stock THF solution of $LiBEt_3H$ (Aldrich Super-Hydride) to a THF slurry of (dippp)$PdCl_2$ (dippp = 1,3-bis(diisopropylphosphino)propane) at −40 °C led to the formation of a deep red solution, from which red crystals of the formula $(dippp)_2Pd_2H_2{\cdot}LiBEt_4$ (**1**) could be isolated in approximately 68% yield[8] as shown in Scheme I.

The X-ray crystal structure[9] of **1** is also shown in Scheme I. The binuclear structure is clearly evident as are the bridging

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[§] Killam Postgraduate Scholar, 1989–1990.

[∥] Professional Officer: UBC Crystallographic Service.

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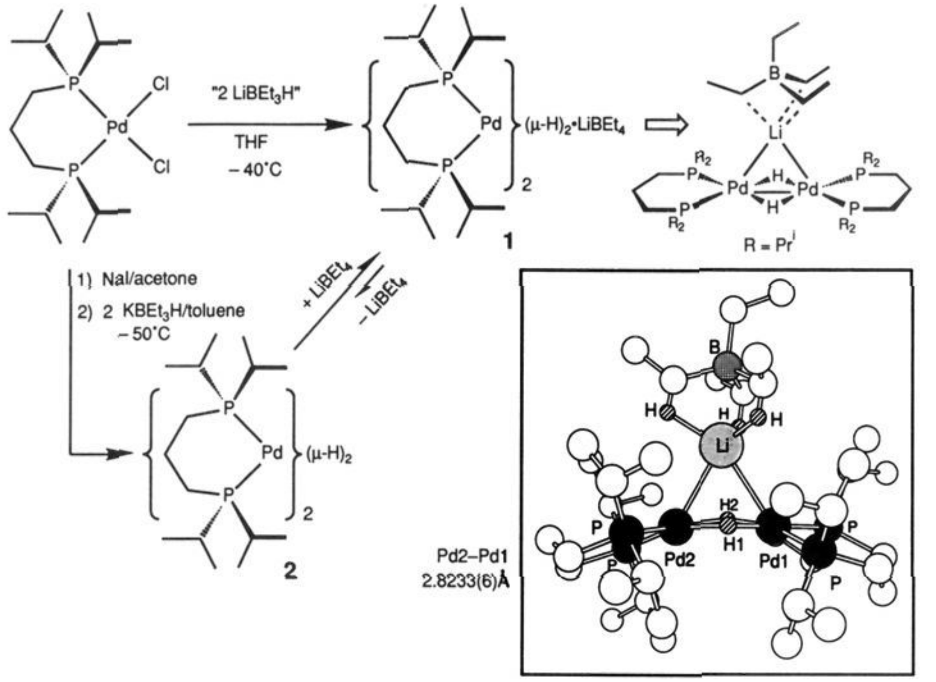
(8) ^1H NMR (ppm, C_6D_6): δ 1.78 (br m, 6 H), 1.29 (m, 10 H), 1.20 and 1.07 (m, 24 H), 0.42 (br m, 4 H), −3.66 (br quin, 1 H). $^{31}P\{^1H\}$ NMR (ppm, C_6D_6): δ 22.4 (br s). Anal. Calcd for $C_{38}H_{90}BLiP_4Pd_2$ (found): C, 50.62 (50.57); H, 10.06 (10.06).

(9) Crystals of $[(dippp)Pd]_2(\mu\text{-}H)_2{\cdot}LiBEt_4{\cdot}0.5(C_6H_{14})$ are monoclinic, a = 11.531 (2) Å, b = 19.105 (4) Å, c = 24.002 (4) Å, β = 98.64 (2)°, Z = 4, D_{calcd} = 1.200 g cm^{-3}, space group $P2_1/n$. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to R = 0.033 and R_w = 0.037 for 5948 reflections with $I \geq 3\sigma(I)$. Full details of the crystallographic analysis are included as supplementary material.

Scheme I



hydrides which were located and refined. The palladium–hydride bond lengths range from 1.62 (5) to 1.79 (4) Å (cf.: Pd(1)–H(1), 1.62 (5) Å; Pd(1)–H(2), 1.62 (5) Å; Pd(2)–H(1), 1.78 (4) Å; Pd(2)–H(2), 1.79 (4) Å; the Pd–H–Pd angle is 112 (3)°. However, the most interesting feature of this structure is the presence of a coordinated $LiBEt_4$ unit having the lithium sandwiched between the $Pd_2(\mu\text{-}H)_2$ core and the BEt_4 anion. The palladium–lithium distances are significantly different, with the lithium being closer to Pd(2): Pd(1)–Li, 2.737 (8) Å, and Pd(2)–Li, 2.639 (8) Å. Also noteworthy is the interaction of the lithium with the BEt_4 unit as the lithium binds to the C–H bonds of the α-carbon of the ethyl substituents; the Li–H bond distances range from 1.70 to 1.85 Å. The neutron diffraction study of $LiBMe_4$ shows similar Li–H–C interactions, but in this case the Li–H bond distances are somewhat longer, ranging from 2.01 to 2.21 (5) Å.[10]

Two questions needed to be addressed: (i) Where did the $LiBEt_4$ originate? (ii) How strongly was it bound to the palladium dimer? The first point was easily resolved by analysis of our stock solution of Super-Hydride from Aldrich. Fortuitously, instead of having a solution of $LiBEt_3H$ in THF, our particular bottle contained roughly an equal amount of $LiBEt_2H_2$ and $LiBEt_4$ as determined by ^{11}B NMR.[11] To answer the second question, we prepared the parent palladium hydride dimer $[(dippp)Pd]_2(\mu\text{-}H)_2$ (**2**[12]) by reaction of the diiodide with 2 equiv of crystalline $KBEt_3H$ in toluene (Scheme I).

In analogy to the corresponding nickel dimers, the structure of **2** is assumed to have the two Pd(dippp) ends staggered with respect to each other.[13] Addition of stoichiometric amounts of solid $LiBEt_4$ to a benzene or toluene solution of the parent hydride dimer **2** immediately produced the $LiBEt_4$ adduct **1** as determined by $^{31}P\{^1H\}$ NMR spectroscopy ($K > 500$ at 25 °C). Examination of the crude reaction mixture obtained by reaction of the THF solution of $LiBEt_2H_2$ and $LiBEt_4$ with $(dippp)PdCl_2$ showed that the parent hydride-bridged dimer **2** was the initial product and that the adduct **1** formed only after removal of THF. Adduct formation is undoubtedly hindered initially because of the presence of THF which can coordinate to Li^+. Extension of other lithium salts is underway; for example, addition of $LiAlEt_4$ to the palladium hydride dimer **2** also produces the corresponding adduct $[(dippp)Pd]_2(\mu\text{-}H)_2\cdot LiAlEt_4$.[14]

In this paper we have presented the first example of a well-defined hydride-bridged dimer of palladium which has been crystallographically characterized. From this work palladium complexes that have bridging ligands would appear to be accessible via standard procedures; however, the importance of the bulky chelating phosphine ligand is yet to be determined.[15] The most important aspect of this report is the observation that adducts can form between the palladium hydride dimer and certain lithium salts. Such an interaction between Li^+ (as a salt) and a hydride-bridged dimer is unprecedented.[16] Also noteworthy from the X-ray structure is the interaction of the Li cation with the BEt_4 anion; in the absence of coordinating solvents, the Li^+ binds to three α-carbon hydrogens (and the electron-rich $Pd_2(\mu\text{-}H)_2$ core).[17] Attempts to understand the bonding in this interaction and extend this type of adduct are underway.

Acknowledgment. Financial support from NSERC of Canada (operating grants to M.D.F and postdoctoral fellowship to B.R.L.) and the Izaak Walton Killam Foundation (postgraduate scholarship to G.K.B.C.) is gratefully acknowledged. We also thank Johnson-Matthey for the generous loan of Pd salts.

Supplementary Material Available: Full details of the preparation of all of the complexes and the crystal structure analysis

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[11] ^{11}B NMR of the contents of our Super-Hydride bottle gave two resonances δ −17.5 (s) and −17.8 (t, $J = 67.4$ Hz), attributed to $LiBEt_4$ and $LiBEt_2H_2$, respectively. Other bottles examined were found to contain only $LiBEt_3H$. For another example of this, see ref 11 in the following: Thaler, E.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1987**, *26*, 374.

[12] ^1H NMR (ppm, C_6D_6): δ 1.93 (m, 6 H), 1.30 (m, 4 H), 1.30 and 1.10 (m, 24 H), −2.52 (quin, 1 H, $J = 34.9$ Hz). $^{31}P\{^1H\}$ NMR (ppm, C_6D_6): δ 27.0 (s). Anal. Calcd for $C_{30}H_{70}P_4Pd_2$ (found): C, 46.94 (47.22); H, 9.19 (9.25).

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[14] ^1H NMR (ppm, C_6D_6): δ 1.75 (br m, 6 H), 1.21 (m, 6 H), 1.16 and 0.97 (m, 28 H), 0.89 (br m, 4 H), −3.87 (br quin, 1 H). $^{31}P\{^1H\}$ NMR (ppm, C_6D_6): δ 23.3 (br s). Anal. Calcd for $C_{38}H_{90}AlLiP_4Pd_2$ (found): C, 49.73 (49.48); H, 9.88 (9.85).

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of **1** and tables of crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes for **1** (24 pages); listing of observed and calculated structure factors for **1** (81 pages). Ordering information is given on any current masthead page.

Why Does Tetrafluoroethylene Not Undergo Diels–Alder Reaction with 1,3-Butadiene? An ab Initio Investigation

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Although the reaction of ethylene with 1,3-butadiene yields a trace of vinylcyclobutane,[1] by far the major product (99.98%) is cyclohexene, the product of a concerted Diels–Alder reaction.[2] In contrast, tetrafluoroethylene (TFE) reacts with 1,3-butadiene to give, as the only isolated product, 1,1,2,2-tetrafluoro-3-vinylcyclobutane,[3] presumably via a stepwise mechanism involving a diradical intermediate.[4] As part of an ongoing study of the effects of fluorine substituents on structure and reactivity,[5] we have investigated computationally whether the four fluorines in TFE destabilize the transition state for the Diels–Alder reaction or stabilize the transition state for diradical formation. We report the results of ab initio calculations which show that while the fluorine substituents in TFE have little effect on the relative energy of the Diels–Alder transition state, they have a profound stabilizing effect on diradical formation.

The transition state for the Diels–Alder reaction of ethylene with butadiene has previously been located by RHF calculations with both the 3-21G[6] and 6-31G*[7] basis sets. We performed RHF calculations with these two basis sets[8,9] in order to locate the transition state for the Diels–Alder addition of TFE to butadiene. The calculations described in this communication were performed with the Gaussian 86[10] and Gaussian 88[11] packages of ab initio programs.

The calculated transition-state geometry for the Diels–Alder reaction of TFE with butadiene[12] is very similar to that reported for the parent Diels–Alder reaction.[6,7] In addition, as shown in Table I, the calculated energy differences between the transition states and the reactants for the two Diels–Alder reactions are also very similar at all levels of theory. Indeed, at the RMP2/6-31G* level of theory the two energy differences are essentially the same.[13] Clearly, the presence of the fluorines in TFE has little effect on the transition state for the concerted Diels–Alder reaction of TFE.

Table I. Calculated Energies at Stationary Points on the $C_2X_4 + C_4H_6$ Potential Energy Surface, Optimized with the 3-21G Basis Set

	energy, hartrees		ΔE,^{a,b} kcal/mol	
level of theory^{c}	X = H (**4**)	X = F (**1**)	X = H (**4**)	X = F (**1**)
	Diels–Alder Transition States			
RHF/3-21G	−231.603 21^{d}	−624.857 31	35.9	36.1
RHF/6-31G*	−232.879 47	−628.251 69	45.1	50.2
RHF/6-31G*^{e}	−232.879 61^{f}	−628.256 28	45.0	49.6
RMP2/6-31G*	−233.677 63	−629.733 17	17.0	16.8
	1,4-Diradical Intermediates^{g}			
UHF/3-21G	−231.652 83	−624.947 77	4.8	−20.7
UHF/6-31G*	−232.943 58	−628.365 65	4.8	−21.3
UMP2/6-31G*	−233.650 19	−629.747 23	34.3	12.5
PUHF/3-21G	−231.667 91	−624.961 94	−4.7	−29.6
PUHF/6-31G*	−232.959 03	−628.380 09	−4.9	−30.4
PUMP2/6-31G*	−233.663 13	−629.759 39	26.1	0.4
ROHF/3-21G	−231.624 42	−624.920 69	22.6	−3.7
GVB/3-21G^{h}	−231.625 27	−624.921 96	22.1	−4.5

^{a} Relative to reactants (C_2X_4 + *s-trans*-1,3-butadiene). ^{b} Uncorrected for zero-point energies. ^{c} Unless otherwise stated, all energies are based on 3-21G optimized geometries (RHF or UHF). ^{d} Reference 6. ^{e} RHF/6-31G* optimized geometry. ^{f} Reference 7a. ^{g} Triplet states. ^{h} Singlet state.

In order to examine the effect of fluorine substituents on the transition state for diradical formation, we have performed UHF/3-21G optimizations of the all-trans conformers of the allylic 1,4-diradical intermediates in the butadiene + TFE and butadiene + ethylene reactions. Previous calculations on tetramethylene[14] and vinyltetramethylene[15] have found that these two diradicals are essentially isoenergetic with the transition states from which they are formed and that closure of these two diradicals to give cyclobutane and vinylcyclobutane, respectively, is inhibited only by small conformational barriers.

We optimized the geometries of the triplet states of the two allylic 1,4-diradicals, since closure and cleavage from the triplet states are spin forbidden. The optimized geometries for the two diradicals[12] are quite similar, with two exceptions: (i) The pyramidalization angle at the nonallylic CX_2 radical center is, as anticipated,[5] substantially larger when X = F than when X = H ($\phi = 46.6°$ versus $\phi = 9.6°$). (ii) The new C–C bond between butadiene and TFE is shorter than the corresponding bond between butadiene and ethylene (R = 1.509 Å versus 1.555 Å). The energies of the two diradicals, relative to the reactants, have been calculated at several different levels of theory and are given in Table I. Comparison of the triplet ROHF and singlet GVB energy of each diradical shows that, as expected for trans-1,4-diradicals,[16] the two electronic states are nearly isoenergetic.

As shown in Table I, the energies of the two diradicals, relative to the reactants from which they are formed, depend on whether electron correlation is included and whether higher spin states are projected from the heavily contaminated (S^2 = 2.23) UHF wave functions of the two triplet diradicals. However, relative to the reactants, *at all levels of theory the 1,4-diradical formed from TFE is 25-26 kcal/mol more stable than the 1,4-diradical formed from ethylene*. The computational finding that fluorine substi-

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[12] Available as supplementary material.

[13] MP2 calculations overestimate the amount by which the correlation energy of the Diels–Alder transition state exceeds that of the reactants, but calculations at the MP4SDTQ level give an activation energy that is very close to the experimentally measured value.[7]

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