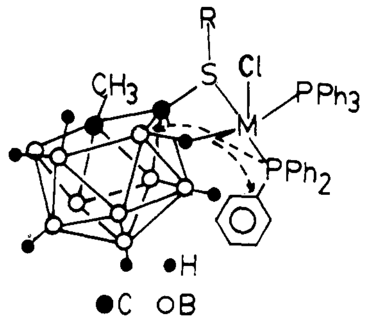

Figure 4. Proposed intermediate in the synthesis of **3**. The dashed lines indicate possible pathways for the P-C cleavage by the activated hydrogen atom and subsequent B-P formation.

reactions are also found in (phosphine)rhodacarborane,[10] (phosphine)ruthenacarborane,[11] and (phosphine)platinacarborane.[12] In these examples a metal-bonded PPh_3 unit migrates and forms a $B\text{-}P(PPh_3)$ bond with the formally B(10) in the free ligand. Since the ^{11}B NMR spectrum of **3** presents a doublet of doublets at -27.2 ppm attributable to a $B(10)\text{-}H_2$ fragment, it may be concluded that B(10) remains unaltered. The absorption at -23 ppm (attributed to B(4) or B(2)) is observed at a considerably higher field than in the free ligand (at least 5 ppm), thus suggesting that either B(4) or B(2) is experiencing a strong effect, probably an "antipodal effect",[13] which is equivalent to considering that the antipodal boron atom (i.e., B(11) if B(4) is taken) has been significantly altered, e.g., by formation of a B-P bond. This favors a P disposition on B(11) or B(9) which is also in agreement with the ^{11}B NMR absorption (B-P) at -8.9 ppm. The subsequent X-ray analysis of **3**[14] clearly establishes the position of the B-P moiety at the B(11) position, but surprisingly, the phosphine is a PPh_2 fragment and not the PPh_3 unit (Figure 3). The Pd is square planar surrounded by $P(PPh_3)$, $P(PPh_2\text{-carbaborane})$, S, and Cl, so that the compound has the formula $PdPPh_3Cl\{7\text{-}SMe\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9\}$ (**3**) which includes the new ligand $\{7\text{-}SMe\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9\}$. Similarly to the *exo*-dithiocarbaborane metal complexes, a five-membered ring is also formed, $\overline{S_a\text{-}M\text{-}P\text{-}B\text{-}C_c}$, which now includes one sulfur and one phosphorus instead of two sulfur atoms. While examples of this kind of bond cleavage and P-B bond formation have already been published, never previously had they been observed in the same compound and under such exceedingly mild conditions. Examples of relatively mild phase-transfer-catalyzed P-C bond cleavage in platinum[15] and iridium[16] have recently been reported, but in all these cases, basic conditions were required. The ligand modification (B-P formation and P-C cleavage) is not restricted to the particular case presented here, but to every R (Figure 2) tested so far ($R = CH_3$, CH_2CH_3, $(CH_2)_3$, $CH_2CH_2C(CH_3)_3$, CH_2Ph). We believe that the system evolves from an initial agostic B(11)-H···M (Figure 4) interaction which enhances the strong hydrido character of the hydrogen. This in turn produces the P-C bond cleavage favored by the formation of the five-membered ring to form a phosphido group[17-23] which couples with the carbaborane cage.

Supplementary Material Available: Tables of bond angles, positional parameters for non-hydrogen atoms, anisotropic thermal coefficients for non-hydrogen atoms, and bond lengths for **3** (10 pages); listing of observed and calculated structure factors for **3** (38 pages). Ordering information is given on any current masthead page.

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Theoretical Calculations on Nb and Ta Trihydride Complexes. Relations with the Problem of Quantum Mechanical Exchange Coupling

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The anomalous NMR properties of some transition metal trihydrides, namely $(C_5Me_5)RuH_3PR_3$ (**1**),[1] $[(C_5H_5)IrH_3PR_3]$[2] (**2**), and $(C_5H_3R'R'')_2NbH_3$ ($R' = R'' = H$ (**3a**); $R' = SiMe_3$, $R'' = H$ (**3b**); $R' = R'' = SiMe_3$ (**3c**))[3] have recently attracted considerable interest. Thus these compounds which adopt a similar geometry implying a coplanar configuration for the hydrides show NMR spectra characterized by AB_2 type patterns for the hydrides but with large temperature-dependent $J_{A\text{-}B}$ coupling constants. The largest observed value is so far 1565 Hz in an iridium complex, well outside the normal range of H-H coupling constants.[2] The physical phenomenon has been clearly identified by two groups[4,5] as due to quantum mechanical exchange of hydrides. However, the chemical origin of these couplings remains unclear. One striking problem was the presence of the anomalous couplings in niobium derivatives of type **3** whereas they were not found in the related isoelectronic and isostructural tantalum compounds $[(C_5H_3R'R'')_2TaH_3$: $R' = R'' = H$ (**4a**); $R' = SiMe_3$, $R'' = H$ (**4b**); $R' = R'' = SiMe_3$ (**4c**)]. The variation of the NMR spectra

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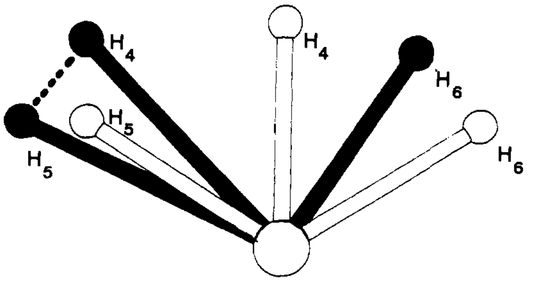

Figure 1. Schematic description and labeling of the H atoms in the C_{2v} (white) and C_s (black) structures.

Table I. Relevant Geometrical Parameters for the C_{2v} Structures[a]

	calc	exp
Ta–H_4	1.70	1.77
Ta–H_6	1.73	1.77
$\angle H_4TaH_6$	61	63
Nb–H_4	1.68	1.65
Nb–H_6	1.72	1.76
$\angle H_4NbH_6$	57	61

[a] Distances are in Å and angles in deg. Experimental values are taken from ref 14.

of Cp_2NbH_3 had been previously discussed in the literature[6] and the observation of very large coupling constants in Lewis acid adducts of this complex reported.[7] The difference between niobium and tantalum was for us reminiscent of the non-classical structure of $RuH_4(PR_3)_3$ or $RuH_6(PR_3)_2$ compared with the classical structure of $OsH_4(PR_3)_3$ or $OsH_6(PR_3)_2$.[8] The presence of a dihydrogen complex could thus play a role. In order to shed some light on the phenomenon, we attempted ab initio calculations on two models of compounds, **3** and **4**, i.e. $[Cl_2NbH_3]$ and $[Cl_2TaH_3]$. This communication describes our preliminary results.

All calculations have been performed at the RHF level using an effective core potential operator for all core electrons. For Cl and C, standard values for the parameters have been used,[9] and for Nb and Ta, new sets have been derived using the Durand and Barthelat method.[10] These parameters have been shown to correctly reproduce the all-electron relativistic results for the orbital energies for both d^3s^2 (^4F) and d^4s^1 (^6D) atomic states. Details about the derivation of the pseudopotential parameters and basis sets will be published elsewhere. The final Gaussian basis set used was of double-ζ quality for C, Cl, and H and of triple-ζ quality for Nb and Ta. The geometry optimization was carried out with the MONSTERGAUSS program[11] and force constant calculations with the PSGRAD program.[12]

Since complete investigation of geometrical structures and force fields was out of scope for the Cp derivatives, we have used models in which cyclopentadienyl ligands are replaced by two Cl, following the suggestion of Steigerwald and Goddard.[13] In a preliminary step we have checked that this modelization does not introduce too severe a bias in the results. The reference geometry was the trihydride C_{2v} structure of the Nb compound for which we have completely optimized the structure for both Cl_2NbH_3 and $(Cp)_2NbH_3$.

Table II. Relevant Geometrical Parameters Optimized for the C_s Structures[a]

	X = Nb	X = Ta
XH_4	2.13	1.85
XH_5	2.14	1.86
XH_6	1.77	1.75
$\angle H_4XH_5$	20.7	17.8
$\angle H_4XH_6$	76.9	73.2

[a] Distances are in Å and angles in deg.

In a second step we have made complete geometry optimization (including calculation of the Hessian matrix) of the model compounds with Nb and Ta, both in C_{2v} (trihydride) and C_s (hydrogen hydride) structures. The results obtained for the C_{2v} structures (see Figure 1) are in very good agreement with the experimental x-ray values[14] (see Table I), taking into account the various approximations made. The most noticeable difference is the central Ta–H distance which we found to be 0.03 Å shorter than the non-central ones (with a similar 0.04-Å shortening in the niobium compound) whereas crystal structure values are almost identical (Cp_2TaH_3: 1.769 (8), 1.775 (9), 1.777 (9) Å; Cp_2NbH_3: 1.65 (6), 1.65 (6), 1.76 (7) Å) for M–H_4, M–H_5, and M–H_6, respectively.

For the C_s structures we clearly obtained a local minimum on the potential energy surface for a hydrogen hydride complex, characterized by a H_4–H_5 distance which is in both compounds very close to the H_2 molecule distance (0.89 Å for Ta and 0.77 Å for Nb). A complete description of the parameters is given in Table II. For the Nb compound, the C_s structure (containing coordinated dihydrogen) is more stable (by 14.6 kcal·mol^{-1}) than the C_{2v} one (trihydride structure), and the reverse is true for the Ta compound (by 7.3 kcal·mol^{-1}). These values calculated at the RHF level are meaningful only as comparisons between the two compounds. These findings are in agreement with the known chemistry of the niobium and tantalum trihydrides. For example, Tebbe, Parshall, et al.[14,15] have shown the greater reactivity of niobium complexes for C–H activation when compared with tantalum complexes. This reaction implies the elimination of H_2 as the first step. Furthermore, hydrogen loss from Cp_2NbH_3 was observed under N_2 at room temperature.[15b]

The model proposed by Zilm et al.[5] to explain the surprisingly large J_{HH} coupling measured in the Nb compound invoked the exchange mechanism between two hydrogen atoms. The strength of this mechanism is linked to the values of the vibrational force constants in a simple two-oscillator model.[16] In order to verify the validity of this hypothesis we have calculated the complete force field at the C_{2v} equilibrium geometry. A very striking feature is the large difference between Nb and Ta regarding the symmetric stretch of the H–H–H distance (ν_{Ta} = 1032 cm^{-1}, ν_{Nb} = 603 cm^{-1}). If we accept, as a first and very crude approximation to identify this vibration with that used by Zilm et al., we obtain, using formula 5 of ref 5, a J_{HH} ratio at $T = 0$ which is equal to

$$J_{HH}^{Ta}/J_{HH}^{Nb} = \left[\frac{A^{Ta}}{A^{Nb}}\right]^{3/2} \exp\left[-\frac{A^{Ta} - A^{Nb}}{2}(a^2 + \lambda^2)\right]$$

where $A = (mk/\hbar^2)^{1/2}$, m is the mass of the vibrating particles, k is the force constant of the vibration, and a is the equilibrium distance. The parameter λ is a characteristic distance introduced by Landesmann[17] that represents the closest approach of the two protons for which the two-particle wave function is zero. Taking the k values determined by the force field calculation and a = 1.65 Å we obtain $J_{HH}^{Ta}/J_{HH}^{Nb} = 2.3 \times 10^{-9}$ in agreement with the

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fact that only scalar coupling is observed in the Ta complexes whereas exchange coupling is predominant in the case of Nb derivatives. A more refined calculation of the vibrational frequencies (including electron correlation) and a more detailed model for the coupling (with a three-dimensional and three-particle treatment) would be needed to give a more quantitative account of the observed phenomena.

In conclusion, two differences clearly appear between the Nb and Ta trihydrides: the existence in the Nb complex of first a thermally accessible dihydrogen state and second a low-frequency vibration which can account for the exchange coupling observations. These two facts seem to be intuitively related and are in agreement with the observed fluxionality at "high temperature" (-100 to +100 °C according to the compounds) of the trihydride complexes exhibiting exchange coupling.[1-3] A dihydrogen intermediate is likely to be involved in the fluxional processes. In contrast, the tantalum derivatives are not fluxional.[3] In order to establish a tighter connection between our two findings a more complete study of the potential surface including electron correlation is needed. Work in this field is presently in progress.

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Metalloporphyrin-Catalyzed Cooxidation of Olefin in the Singlet Oxygenation of Sulfide

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The photooxygenation of sulfides is responsible for the loss of activity of several important enzymes which are damaged in photodynamic action.[1,2] Much attention has been devoted to the structures and reactivities of initially formed reactive intermediates such as persulfoxide **1**, diradical **2**, and thiadioxirane **3** intermediates in singlet oxygenation of sulfides (Scheme I).[3-11] To our knowledge, no interaction between a sulfide-oxygen adduct and a metal ion, however, has been known. Meanwhile, a high-valency iron oxo species as an active oxidant in the cytochrome P-450 mediated monooxygenases is thought to be involved in the model systems employing iron(III) porphyrin and chemical oxidants such as iodosylbenzene[13] (PhIO) and peracids.[14] We report here the first example of an oxygen atom transfer from a peroxidic intermediate generated in singlet oxygenation of sulfide to metal ion affording metal oxo species, which is responsible for epoxidation.

Scheme I

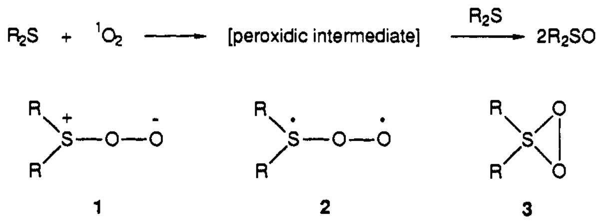
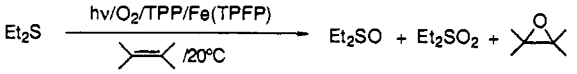


Table I. Cooxidation of Olefin in the Photooxidation of Diethyl Sulfide in the Presence of Fe(TPFP)



run	reactn conditns[a]	olefin (amt, equiv)	Et_2S[b] conv, %	epoxide yield,[c] %	catalyst[d] turnover
1	CH_2Cl_2/2 h	cyclooctene (25)	36	20	23
2	CH_2Cl_2/4 h	cyclooctene (50)	45	30	54
3	C_5H_5N/4 h	cyclooctene (50)	36	14	20
4	no solvent/10 h	cyclooctene (50)	15	20	80
5	CH_2Cl_2/4 h	norbornene (50)	42	48	101
6	CH_2Cl_2/4 h	*cis*-2-heptene (50)	50	28[e]	51
7	CH_2Cl_2/5 h	*trans*-2-heptene (50)	48	5[f]	9
8	CH_2Cl_2/1 h	*cis*-stilbene (100)	75	nd[g]	-
9	CH_2Cl_2/2 h	styrene (50)	64	0.1[g]	(<1)

[a] The ratio of reactants, olefin/sulfide/porphyrin, is 10000/200/1 (run 1 is 3000/120/1, run 8 is 2000/200/1, run 4 is 2000/400/1). Reactions were carried out in 20 mL, porphyrin concentration = 5×10^{-4} M (runs 6 and 7 in 10 mL, porphyrin concentration = 2×10^{-4} M; run 8 in 6 mL, porphyrin concentration = 8×10^{-5} M). [b] In each case, Et_2SO and Et_2SO_2 were also obtained. [c] Yields are based on sulfide consumed; nd is not detected. [d] Epoxide produced/porphyrin used. [e] The ratio of *cis*- and *trans*-epoxide is 82/18. [f] Only *trans*-oxide was obtained. [g] Benzaldehyde was not detected.

In a typical experiment, a dichloromethane solution of diethyl sulfide (8.5×10^{-2} M) and norbornene (50 equiv) was photoirradiated at 20 °C with tetraphenylporphine (TPP, 5.5×10^{-4} M) as sensitizer under an oxygen flow by employing a catalytic amount of (tetrakis(pentafluorophenyl)porphyrinato)iron(III) chloride (Fe(TPFP)). The resulting mixture was subjected to analytical GLC and GC-MS. Norbornene oxide was apparently produced in 48% yield, together with diethyl sulfoxide (90%) and diethyl sulfone (5%) (Table I, run 5). Very similar results were also obtained with cyclooctene (runs 1-4). Control reactions reveal that all of the components, the sulfide, singlet oxygen ($^1O_2$),[15] and Fe(TPFP),[16] are essential for epoxidation. Addition of a radical trap (triphenylmethane) did not have any influence on epoxidation. The results are summarized in Table I.

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