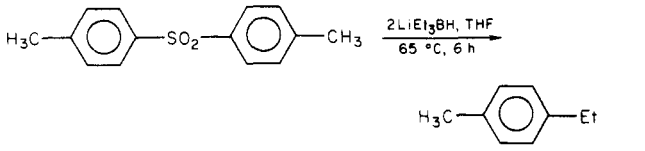
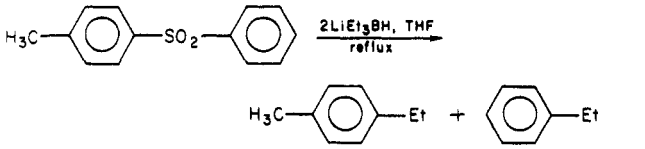


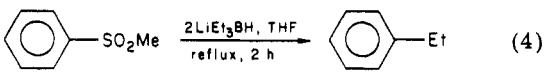
62% (2)

Electron-releasing substituents appear to retard the rate of alkylation, as evidenced by the diminished reactivity of di-*p*-tolyl sulfone. The sensitivity of the reaction to the nature of substituents is also reflected in the ratio of alkylation products realized with the unsymmetrical diaryl sulfone, phenyl *p*-tolyl sulfone (eq 3).



8% 66% (3)

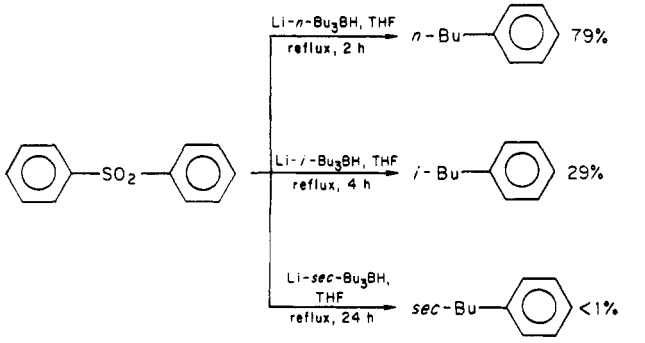
Alkyl aryl sulfones react more sluggishly, giving lower yields of the desired products (eq 4).



(4)

38%

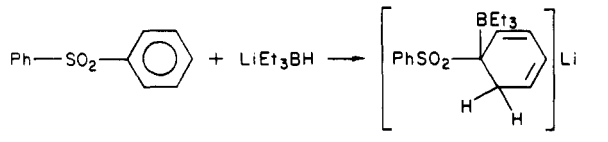
The reaction appears to be general and applicable to other less hindered trialkylborohydrides bearing primary alkyl substituents (*n*-butyl and isobutyl). Even more important, the alkylation proceeds without detectable rearrangement of the carbon skeleton of the alkyl group, a valuable characteristic. The highly hindered reagent, lithium tri-*sec*-butylborohydride (L-Selectride[6]), failed to give any significant amount of *sec*-butylbenzene (eq 5).



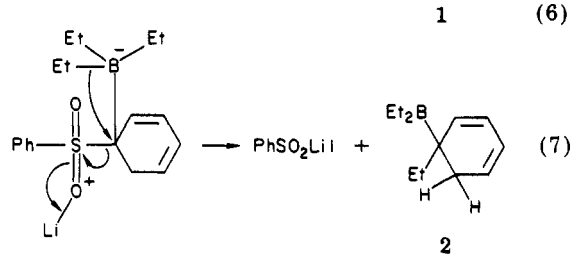
(5)

The reaction appears to involve the following stages, consistent with the above experimental observations (eq 6–8).

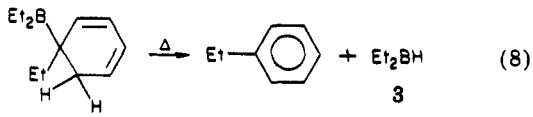
Further, it is possible that the diethylborane (3) thus formed hydroborates the intermediates 1 or 2, thereby lowering the yield of the final product, ethylbenzene. Consequently, trapping the diethylborane produced should enhance the yield of ethylbenzene. Indeed, when the reaction of diphenyl sulfone with lithium triethylborohydride was carried out in the presence of excess 1-octene, the yield of ethylbenzene was increased to 92%; oxidation ($NaOH-H_2O_2$) of the reaction mixture revealed the presence of an equivalent amount of 1-octanol (>99% isomeric purity). Further evidence for the intermediacy of diethylborane was obtained by the conversion of the diethyl alkylborane



1 (6)

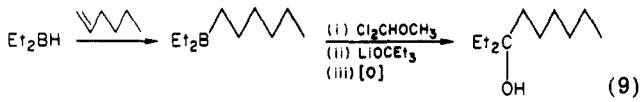


2 (7)



3 (8)

produced to the corresponding tertiary alcohol by the DCME reaction[13] (eq 9).



(9)

In conclusion, the reaction of aryl sulfones with unhindered lithium trialkylborohydride provides the first example of trialkylborohydride mediated carbon–carbon bond formation in aromatic systems. The alkylation proceeds regiospecifically without any rearrangement of the alkyl group.

Registry No. Diphenyl sulfone, 127-63-9; lithium triethylborohydride, 22560-16-3; ethylbenzene, 100-41-4; lithium benzenesulfinate, 16883-74-2; di-*p*-tolyl sulfone, 599-66-6; *p*-ethyltoluene, 622-96-8; phenyl *p*-tolyl sulfone, 640-57-3; methyl phenyl sulfone, 3112-85-4; lithium tributylborohydride, 67335-72-2; lithium triisobutylborohydride, 63717-73-7; butylbenzene, 104-51-8; isobutylbenzene, 538-93-2.

(13) Brown, H. C.; Carlson, B. A. *J. Org. Chem.* **1973**, *38*, 2422–2424.

Homogeneous Catalysis of Hydrogen–Deuterium Exchange Reactions Involving Cyclopentadienyl Complexes of Palladium and Platinum

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Summary: Some cyclopentadienyl complexes of palladium and platinum, when treated with tertiary phosphines, are shown to promote and undergo H–D exchange reactions with a range of deuterated solvents. Two or more routes are involved in the exchange process, one of which depends on base catalysis via zerovalent metal complexes generated during the course of the reactions.

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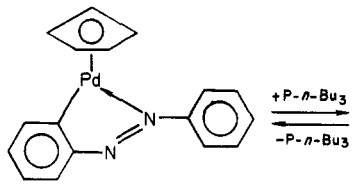
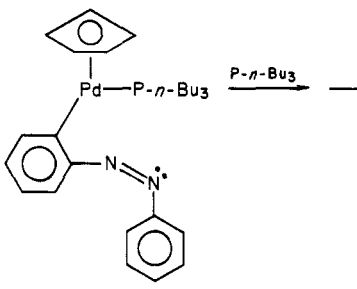
Reactions of cyclopentadienyl complexes of palladium and platinum with tertiary phosphines or other neutral ligands commonly proceed by a $\eta^5 \rightarrow \eta^1$ rearrangement of the cyclopentadienyl group in the absence of a suitable leaving group.[1-3] We have found that in certain deuterated solvents reaction to give zerovalent compounds can occur instead, accompanied by extensive isotopic exchange between the hydrogen atoms of the cyclopentadienyl ring and the solvent.

Our initial studies concerned [Pd(η^5-C_5H_5)(C_6H_4N=NC_6H_4)] (I).[4] Treatment of I in toluene-d_8 with 1 mol equiv of P-*n*-Bu_3 resulted in an 80% reduction in intensity of the cyclopentadienyl resonance at δ 5.65 and the appearance of a doublet at δ 5.80 (J(P,H) = 1.5 Hz). This doublet gradually diminished to zero intensity over 24 h, while the original singlet regained ca. 75% of its former intensity. Successive applications of P-*n*-Bu_3 to a total of 4 or more mol equiv resulted in the final disappearance of the cyclopentadienyl resonances from the ^{1}H NMR spectra. These observations may be explained in terms of eq 1, coordination of P-*n*-Bu_3 being



I



II

(1)

reversible due to the ability of the nitrogen atom to reattack the metal center,[5] and the liberated P-*n*-Bu_3 is ultimately consumed in forming [Pd(P-*n*-Bu_3)$_4$].

The tertiary phosphines PMe_2Ph, $PMePh_2$, and PPh_3 had similar effects on I, although the cyclopentadienyl resonances were broad, indicating that phosphine exchange occurs at a rate comparable with the NMR time scale.[5] Addition of 4 mol equiv of $PMePh_2$ to I allowed isolation of [Pd($PMePh_2$)$_4$] as yellow crystals (Calcd: C, 68.90, H, 5.78. Found: C, 68.91, H, 5.62.) Similar eliminations of organic groups from Pd(II) or Pt(II) complexes by tertiary phosphines to generate zerovalent species are well documented.[6,7] Unless the reactions are performed under anaerobic conditions, the tertiary phosphine is steadily oxidized, catalyzed by [Pd(PR_3)$_4$].[8]

When the reactions were performed in $CDCl_3$ solution, the ^{1}H NMR spectra exhibited a sharp singlet at δ 7.25 due to $CHCl_3$, as well as the resonances associated with [Pd(η^5-C_5H_5)(C_6H_4N=NC_6H_5)(PR_3)] (II). The concentration of $CHCl_3$ increased over several hours, whereas the signals due to the cyclopentadienyl groups diminished. The efficiency with which the tertiary phosphines produced $CHCl_3$ decreased in the same order as their ability to form II, namely, P-*n*-Bu_3 > PMe_2Ph > $PMePh_2$ > PPh_3. This parallels the order of decreasing nucleophilicity.[9] That the H–D exchange process involves the C_5H_5 ring protons was shown by the reaction of [Pd(η^5-C_5D_5)(C_6H_4N=NC_6H_5)][10] with P-*n*-Bu_3 in $CHCl_3$. This resulted in a signal at δ 5.90, which may be assigned to the protonated complex I.

Reactions of I with $PMePh_2$ in a range of deuterated solvents gave the following order for the extent of proton incorporation into the solvent, as measured by ^{1}H NMR spectroscopy: $CD_3CN \approx (CD_3)_2CO > CDCl_3 > CD_2Cl_2 \gg C_6D_5CD_3 = 0$. In addition, any moisture present in the solvents became involved in the exchange reactions. Moreover, addition of 2 drops of D_2O to a NMR tube containing an acetone-d_6 solution of I greatly enhanced the rate and degree of H–D exchange on P-*n*-Bu_3 addition. On the other hand, reaction of I with P-*n*-Bu_3 in rigorously dried $CDCl_3$ resulted in no H–D exchange. It may be noted that the solvent sequence above approximately follows their pK_a values[11] and also reflects their diminishing propensity to absorb moisture. We believe both to be critical factors.

In a number of experiments, production of protonated solvents continued after the cyclopentadienyl resonances had disappeared or reached a steady intensity. This indicates that at least two independent processes are involved, not all of which involve analogues of compounds I or II.

One process undoubtedly utilizes zerovalent palladium complexes, generated in the course of reaction 1. In support of this, we have found [Pd(P-*n*-Bu_3)$_3$] or [Pd($PMePh_2$)$_4$], prepared from [$Pd_2(\mu$-Cl)$_2(\eta^3$-$C_3H_5)_2$] and PR_3,[6] to be active catalysts in a number of H–D exchange reactions involving organic compounds and D_2O. Such complexes are expected to react with water to produce hydridopalladium species and hydroxide ions,[12] which initiate base-catalyzed exchange reactions. Base catalysis as a H–D exchange mechanism is well-known,[13] and it explains the observed dependence on solvent acidity. Related exchange reactions between ketones and D_2O, catalyzed by platinum(0) complexes, have been reported.[14] The reversible formation of II, and its analogues, ensures that [PdL_n] is formed even when only 1 equiv of tertiary phosphine is added to I.

A number of possibilities exist for the alternative process(es) involving the cyclopentadienyl protons. Elimination of the $C_5H_5^-$ anion from II upon further attack of P-*n*-Bu_3 could initiate the base-catalyzed H–D exchange sequence, and, indeed, the elimination may be reversible. Such an elimination has not been previously proposed, but

(1) Cross, R. J.; Wardle, R. *J. Chem. Soc. A* **1971**, 2000.
(2) Tune, D. J.; Werner, H. *Helv. Chim. Acta* **1975**, *58*, 2240.
(3) Goel, A. B.; Goel, S.; Van Der Veer, D.; Clark, H. C. *Inorg. Chim. Acta* **1981**, *53*, L117.
(4) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272.
(5) Cross, R. J.; Tennent, N. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1444.
(6) Kuran, W.; Musco, A. *Inorg. Chim. Acta* **1975**, *12*, 187.
(7) Mukhedkar, A. J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 3023. Clark, H. C.; Itoh, K. *Inorg. Chem.* **1971**, *10*, 1707. Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1310.
(8) Cook, C. D.; Jauhal, G. S. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 31. Birk, J. P.; Halpern, J.; Pickard, A. L. *J. Am. Chem. Soc.* **1968**, *90*, 4491.
(9) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(10) Anderson, G. K.; Cross, R. J.; Phillips, I. G. *J. Chem. Soc., Chem. Commun.* **1978**, 709.
(11) Cram, D. J. "Organic Chemistry"; Blomquist, A. T., Ed.; Academic Press: New York, 1965; Vol. 4.
(12) These probably exist as ion pairs, since conductance measurements have indicated that free ions are not involved in the case of palladium.[14]
(13) Thomas, A. F. "Deuterium Labelling in Organic Chemistry"; Appleton Century Crofts: New York, 1971.
(14) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027.

a similar displacement of β-diketonate anions from palladium(II) has been observed to cause H–D exchange with $CDCl_3$.[15] This route can successfully explain the formation of protonated cyclopentadienyl complexes from the deuterated starting material, and the observed dependence on water concentration, since base catalysis is again involved.

A second possibility is transfer of a hydride from the cyclopentadienyl ring to palladium. This could also result in H–D exchange, such a process perhaps being facilitated by phosphine migration to the ring.[16] Formation of a hydridopalladium species by this route should be reversible and could cause complete deuteration of the cyclopentadienyl ring. Alternatively, protonation of the cyclopentadienyl ring and elimination of cyclopentadiene could in principle occur, although this is unlikely to be reversible and no obvious proton source is available.

Finally, it is possible that some (though not all) of the H–D exchange involving the ring protons is catalyzed by $[PdL_n]$. Addition of 0.17 mol equiv of $[Pd(P\text{-}n\text{-}Bu_3)_3]$ to a solution of I in acetone-d_6/D_2O caused almost quantitative exchange within the cyclopentadienyl ring, while the appearance of signals at δ 2.10 (quintet) and 3.50 (br s) indicated the formation of CHD_2COCD_3 and HOD (or H_2O), respectively. The fact that H–D exchange between water and the solvent has been observed to proceed independently of any change in cyclopentadienyl proton intensity, however, means that such a route for exchange of the ring protons could not be fast compared to the other process(es) involving the ring. Indeed, during the deuteration of I in the presence of $[Pd(P\text{-}n\text{-}Bu_3)_3]$ II was also observed, indicating that P-*n*-Bu_3 dissociation occurs, thereby opening the way for alternative mechanisms to operate here also.

Investigations of other cyclopentadienyl systems are being undertaken at present. Addition of tertiary phosphines to solutions of $[Ni(\eta^5\text{-}C_5H_5)(C_6H_4N{=}NC_6H_5)]$ did not result in any isotopic exchange, but $[Pd(\eta^5\text{-}C_5H_5)(C_6H_5)(P\text{-}n\text{-}Bu_3)]$ reacted with P-*n*-Bu_3 in deuteriochloroform to yield some protonated solvent. A series of complexes $[Pt(\eta^5\text{-}C_5H_5)R(PR^1{}_3)]$ also reacted with $PR^1{}_3$ to give $CHCl_3$, the rate of H–D exchange decreasing in the orders $PR^1{}_3$ = PMe_2Ph > $PMePh_2$ and R = *p*-$Me_2NC_6H_4$ > *p*-$MeOC_6H_4$ > C_6H_5 > $CCl{=}CCl_2$.

These reactions present some interesting possibilities for the generation of deuterated or partially deuterated organic and organometallic molecules under very mild conditions, as well as providing an approach to the activation of water toward synthetically useful reactions, and work is currently in progress in these directions.

Acknowledgment. Thanks are expressed to Johnson Matthey for generous loans of palladium salts, and the award of a Faculty Research Fellowship by the University of Missouri—St. Louis (G.K.A.) is gratefully acknowledged.

Registry No. I, 85453-00-5; $Pd(PMePh_2)_4$, 24981-80-4; P-*n*-Bu_3, 998-40-3; PMe_2Ph, 672-66-2; $PMePh_2$, 1486-28-8; PPh_3, 603-35-0; H_2O, 7732-18-5; $Pd(P\text{-}n\text{-}Bu_3)_3$, 52359-13-4; $Pd(PMePh_2)_4$, 24981-80-4.

(15) Okeya, S.; Nakamura, Y.; Kawaguchi, S. *J. Chem. Soc., Chem. Commun.* **1977**, 914; *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3396.
(16) See, for example: Munro, G. A. M.; Pauson, P. L. *J. Chem. Soc., Chem. Commun.* **1976**, 134.

Synthesis and Decarboxylation Mechanism of the Chiral Rhenium Formate $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)$

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Summary: Formate $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)$ (**1**) decarboxylates to $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**2**) without PPh_3 dissociation, with retention at rhenium, with k_H/k_D (112 °C) = 1.55 ± 0.19, $\Delta H^\ddagger$ = 26.8 ± 0.6 kcal/mol, and $\Delta S^\ddagger$ = −6.3 ± 1.3 eu.

Catalyst-bound formates have been proposed as intermediates in some water gas shift reactions,[3,4] the iridium-catalyzed isomerization of methyl formate to acetic acid,[5] transfer hydrogenations involving formate ion,[6] metal-catalyzed decarboxylations of formic acid,[7] and CO_2/H_2 reactions.[8] Consequently, the chemistry of transition-metal formate complexes has been of intense recent interest.[4,9] In this communication, we report the synthesis of the first optically active formate complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)$ (**1**) and mechanistic details on its decarboxylation to hydride $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H)$ (**2**).

Reaction of racemic $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$[10] (**3**) with 1.5 equiv of 88% aqueous HCO_2H in CH_2Cl_2 at −24 °C gave, after workup and CH_2Cl_2/hexane recrystallization, red needles of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(OCHO)\cdot 0.75CH_2Cl_2$ ($1\cdot 0.75CH_2Cl_2$) in 79% yield (eq 1). Subsequent rapid CH_2Cl_2/hexane precipitation gave solvate free **1**. The presence of the formate ligand was indicated by a ^1H NMR resonance at δ 8.06, a ^{13}C NMR resonance at 171.4 ppm, and IR $\nu_{C=O}$ at 1616 (s) and $\nu_{H\text{-}CO_2}$ at 2850 (w,

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(2) Address correspondence to this author at the University of Utah. Fellow of the Alfred P. Sloan Foundation (1980–1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980–1985).
(3) (a) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941. (b) King, A. D., Jr.; King, R. B.; Yang, D. B. *Ibid.* **1981**, *103*, 2699. (c) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *Ibid.* **1981**, *103*, 3411. (d) Slegeir, W. A. R.; Sapienza, R. S.; Rayford, R.; Lam, L. *Organometallics* **1982**, *1*, 1728.
(4) (a) Darensbourg, D. J.; Fischer, M. B.; Schmidt, R. E., Jr.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297. (b) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *Ibid.* **1981**, *103*, 3223. (c) Darensbourg, D. J.; Rokicki, A. *Ibid.* **1982**, *104*, 349. (d) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685. (e) Darensbourg, D.; Kudaroski, R. A. *Adv. Organomet. Chem.*, in press.
(5) Pruett, R. L.; Kacmarcik, R. T. *Organometallics* **1982**, *1*, 1693.
(6) Bar, R.; Sasson, Y.; Blum, J. *J. Mol. Catal.* **1982**, *16*, 175.
(7) (a) Strauss, S. H.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1979**, *174*, C59, and references therein. (d) Madix, R. J. *Adv. Catal.* **1980**, *29*, 1.
(8) (a) Ramaroson, E.; Kieffer, R.; Kienneman, A. *J. Chem. Soc., Chem. Commun.* **1982**, 645. (b) Certain data have also been intepreted as evidence for formates in the Cu/ZnO- or ZnO-catalyzed conversion of CO/H_2 to methanol: Ueno, A.; Onishi, T.; Tamaru, K. *Trans. Faraday Soc.* **1971**, *67*, 3585. Klier, K. *Adv. Catal.* **1982**, *31*, 243.
(9) (a) Shapley, J. R.; St. George, G. M.; Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1982**, *21*, 3295. (b) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1982**, *234*, C5. (c) Poonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 3529. (d) Slater, S. G.; Lusk, R.; Schumann, B. F.; Darensbourg, M. *Organometallics* **1982**, *1*, 1662. (e) Roberts, D. R.; Geoffroy, G. L.; Bradley, M. G. *J. Organomet. Chem.* **1980**, *198*, C75.
(10) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

0276-7333/83/2302-0782$01.50/0