Table I. Mössbauer Data

Temp, °K	ΔE_Q, mm/sec	δ,[a] mm/sec	Γ_1,[b] mm/sec	Γ_2,[b] mm/sec	Area[c] ratio	Peak height[c] ratio
RT[d]	1.00	0.33	0.311 ± 0.010	0.263 ± 0.009	1.13	1.34
78	1.03	0.44	0.266 ± 0.005	0.264 ± 0.005	1.03	1.04

[a] Relative to natural iron foil. [b] The error limits are the standard deviations as calculated from the variance of the line width. [c] Ratio of line with least shift to line with largest shift from zero velocity. [d] RT = room temperature.

for a five-coordinate mononuclear complex of iron with *N,N′*-ethylenebis(salicylideneiminate).[11] The most striking features of the Mössbauer spectrum are the distinct asymmetry exhibited by the two lines split by the quadrupole interaction at room temperature and the decrease in this asymmetry with decreasing temperature. It is apparent from Table I that although the temperature dependence is consistent with the Karyagin[12] asymmetry the line-width considerations are not. The line width for each line at 78°K is essentially the same, but at room temperature the line of most positive velocity is distinctly broadened. Thus, it would appear that the Karyagin effect cannot account for the asymmetry in the line widths at room temperature but may be responsible for the small asymmetry observed at 78°K. The observed asymmetry at room temperature could result from spin–spin relaxation effects.[13]

The magnetic susceptibility of the dimer was studied as a function of temperature; in Figure 2 the measured values of μ_{eff} are compared with values calculated[14] assuming antiferromagnetic spin–spin exchange between two high-spin iron(III) ions. The experimental results are best fit with $g = 2.00$, $J = -17.0 \pm 0.6$ cm^{-1}, $N(\alpha) = 0$, and $S = {}^5/_2, {}^5/_2$; the experimental results are not consistent with the spin–spin interaction between two iron(III) ions of lower spin multiplicity.

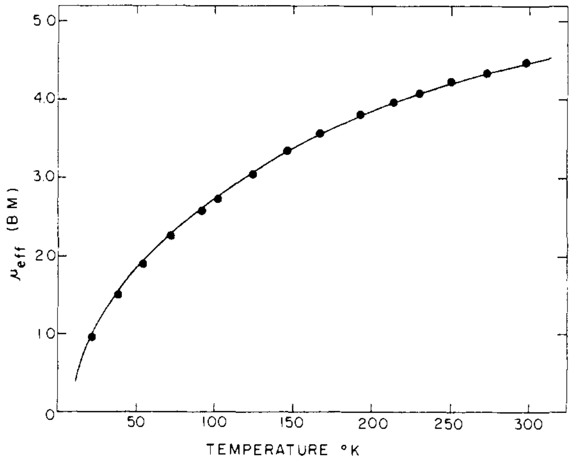


Figure 2. Plot of μ_{eff} *vs.* temperature (●, experimental points; calculated for $J = -17$ cm^{-1}, $g = 2.00$, $N\alpha = 0$, and $S = {}^5/_2, {}^5/_2$).

For the oxygen-bridged iron(III) complexes for which magnetic data and X-ray data are available there appears to be a correlation between the extent of spin–spin interaction and the coordination of the bridging oxygen: for a complex with a linear two-coordinate oxygen[2], $J = -100$ cm^{-1};[10] for a complex with planar three-coordinate oxygens, $J = -17$ cm^{-1} for the complex reported in this paper; and $J = -7$ cm^{-1} [10] for a complex with pyramidal three-coordinate oxygens.[8] Hence, it would appear that the extent of spin–spin exchange can be related directly to the availability of π orbitals on the bridging oxygen.

Acknowledgments. This work was supported in part by NSF Grant No. GP-8475. The computational help of the Rich Electronic Computer Center of Georgia Institute of Technology is appreciated. G. J. L. wishes to thank the NSF for Graduate Research Equipment Grant No. GP-8653 and Project Themis Grant No. AFOSR F-44620-69-C-0122 for the purchase of components for the Mössbauer spectrometer.

---

(11) M. Gerloch and F. E. Mabbs, *J. Chem. Soc. A*, 1598 (1967).

(12) S. V. Karyagin, *Dokl. Akad. Nauk SSSR*, **148**, 1102 (1963).

(13) M. Blume, *Phys. Rev. Lett.*, **14**, 96 (1965).

(14) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

(15) Address correspondence to this author.

J. A. Bertrand,[15] J. L. Breece, A. R. Kalyanaraman
School of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

G. J. Long
Department of Chemistry, University of Missouri—Rolla
Rolla, Missouri 65401

W. A. Baker, Jr.
Department of Chemistry, Syracuse University
Syracuse, New York 13210

Received June 6, 1970

Catalysis of Aromatic Hydrogen–Deuterium Exchange by Metal Hydrides

Sir:

The exchange of hydrogen between water and aromatic hydrocarbons is catalyzed by strong acid,[1] by heterogeneous catalysts, and by a homogeneous system based on the $PtCl_4^{2-}$ ion.[2] In contrast, homogeneous catalytic exchange between gaseous hydrogen and a free aromatic hydrocarbon is unknown even though activation of *o*-H in aromatic phosphorus ligands is well established[3] for a number of transition metals. We now wish to report that the hydrides I–IV catalyze exchange between D_2 and benzene, probably by oxidative addition of the C–H bond to a coordinatively unsaturated intermediate.

$(\pi\text{-}C_5H_5)_2TaH_3$
I

L_2IrH_5
II, L = $PhPEt_2$
III, L = Et_3P
IV, L = Me_3P

Dicyclopentadienyltantalum trihydride (I),[4] like $(Ph_3P)_2ReH_7$, as reported earlier by Chatt and Coffey,[5]

---

(1) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962.

(2) R. I. Hodges and J. Garnett, *J. Phys. Chem.*, **73**, 1525 (1969), and references cited therein.

(3) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

(4) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

Table I. Catalysis of HD Exchange by Metal Hydrides[a]

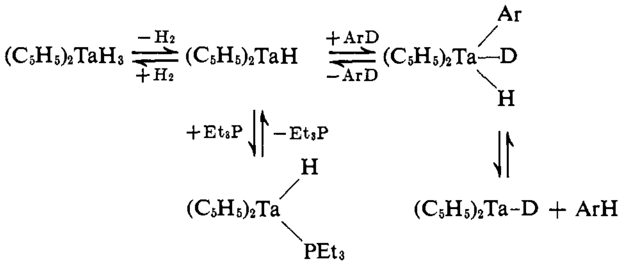
					Gas analysis					
					Theory[b]			Found		
Expt	Complex (mmol)	Solvent	Gas (mmol)	Temp, °C	H_2	HD	D_2	H_2	HD	D_2
A	I (0.16)	C_6D_6	H_2 (0.15)	100				41.4	41.6	17.0
B	II (0.11)	C_6H_6	D_2 (0.08)	25	74.1	24.0	1.9 (9)	72.6	24.8	2.6
C	II (0.11)	C_6H_6	D_2 (0.08)	100	92.2	7.7	0.15 (35)	98.5	1.5	
D	II (0.095)	C_6D_6	H_2 (0.46)	100				10	38	52
E[c]	II (0.095)	C_7H_8	D_2 (0.49)	100	21.7	49.8	28.5 (9)	62.5	32	5.6
F	$(PhPEt_2)_3IrH_3$ (0.093)	C_6H_6	D_2 (0.49)	100	4.84 21.0	34.3 49.7	60.8 (3) 29.3 (9)	8.8	38	53.2

[a] These experiments were carried out in sealed glass ampoules of 4- or 15-ml capacity to give an H_2 or D_2 pressure of about 1 atm. The amount of solvent used in each was 2 ml, and the standard heating period was 24 hr. [b] Calculated for statistical exchange of D_2 with the number of ligand hydrogen atoms per molecule indicated in parentheses. [c] Mass spectrum of the toluene indicates *ca.* 1% toluene-d_1 over the natural abundance.

undergoes exchange of metal–hydrogen with C_6D_6. However, the interaction we have observed is more complex than that reported for the rhenium hydride. When a C_6D_6 solution of I is heated under a hydrogen atmosphere, HD and D_2 appear in the vapor phase (Table I, experiment A). Under these conditions, deuterium could only come from the solvent. Its presence definitely indicates catalytic exchange.

Similar catalysis of exchange between H_2 and C_6D_6 or between D_2 and C_6H_6 was observed with the iridium hydrides II,[6] III,[6] and IV.[7] Exposure of a C_6H_6 solution of II[6] to D_2 for 24 hr at 25° results in statistical exchange of nine hydrogens per molecule of iridium complex (experiment B), a value which corresponds to reaction of the five Ir–H and four *o*-C–H bonds. However at 100° more H_2 and HD were present in the gas phase than could be accounted for even if every hydrogen in the complex equilibrated with the gas phase (experiment C). As with $(C_5H_5)_2TaH_3$, the inverse experiment in deuteriobenzene with H_2 as the exchanging gas gave a substantial amount of HD and D_2 after 24 hr at 100° (experiment D). Exchange with solvent also occurs with toluene (experiment E). The six-coordinate complex *mer*-$(PhPEt_2)_3IrH_3$[6] exchanges slightly more than three hydrogens after 24 hr at 100°, a substantial decline in activity for ligand exchange (experiment F).

In benzene solution the iridium hydrides II–IV decompose spontaneously with evolution of hydrogen, but no metal is deposited.[8] When I is heated under N_2 in benzene at 80° for 15 hr, H_2 is detected in the gas phase. Heating I in benzene with excess Et_3P produces a red crystalline solid whose nmr spectrum[9] indicates that it should be formulated as $(\pi\text{-}C_5H_5)_2Ta(H)PEt_3$. The conversion to the new product is low in a sealed tube but is complete under a N_2 sweep in refluxing toluene. This result suggests that an equilibrium exists between the phosphine hydride and the trihydride. This new complex also catalyzes the exchange of D_2 with benzene. The thermal evolution of hydrogen from these complexes coupled with the exchange data suggest the existence of the equilibria illustrated for the tantalum complex.



Similar equilibria are presumed to occur with the iridium hydrides.

No evidence is presently available concerning the intermediate formed by oxidative addition of an aromatic C–H bond. Aryl hydride complexes have been reported,[10] and a tautomerism between $Ru(dmpe)_2$-$C_{10}H_8$ and $HRu(dmpe)_2C_{10}H_7$ (dmpe = bis-1,2-dimethylphosphinoethane) was observed.[10] Garnett and Hodges[2] have also postulated an analogous addition product in their exchange mechanism. Such an intermediate could have great importance, for it provides an aromatic ring which is susceptible to electrophilic substitution.

(5) J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1963 (1969).

(6) B. E. Mann, C. Masters, and B. L. Shaw, *Chem. Commun.*, 703 (1970).

(7) Prepared by $LiAlH_4$ reduction of $Me_3PH^+[IrCl_4(Me_3P)_2]^-$ in THF and isolated by sublimation from the residue which remains after evaporation of solvent from the hydrolysate. The ^1H nmr spectrum in toluene consists of two triplets in the rato 18:5.5 at τ 8.26 (J_{P-CH_3} = 4 Hz) and 19.73 (J_{P-IrH} = 14 Hz). The ^{31}P nmr consists of a symmetrical sextet (0.94:5:10) at +192.1 ppm from external trimethyl phosphite. The infrared spectrum shows a strong broad absorption at 1920 cm^{-1} for ν_{IrH}.

(8) A number of new hydride resonances are observed in the nmr spectra of these solutions after decomposition. The compositions of these products are being studied.

(9) The proton nmr spectrum in C_6D_6 at 220 MHz shows cyclopentadienyl absorption at τ 5.68 as a doublet of doublets (J_{PH} = 1.7, J_{HH} = 0.5 Hz), a five-line CH_2 signal (overlapping quartets, $J_{PH} \approx 7$, J_{HH} = 7.5 Hz) at τ 8.91, a five-line CH_3 signal (overlapping triplets, J_{PH} = 13.5 Hz) at τ 9.16, and TaH absorption at τ 19.48 (J_{PH} = 21 Hz). The relative intensity ratio $C_5H_5:C_2H_5:TaH$ is 10:15.5:0.9.

(10) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

(11) Address correspondence to this author.

E. K. Barefield, G. W. Parshall,[11] F. N. Tebbe
Contribution No. 1712, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received June 16, 1970

Electron Spin Resonance Study of Dialkylamino Free Radicals in Solution[1]

Sir:

It is generally accepted that the most stable conformation of simple alkyl free radicals is a planar, sp^2 hybridized form with the unpaired electron located in

(1) Acknowledgment is made to the Kansas State University Bureau of General Research for support of this work.