Reductive Coupling of Aralkyl Halides by Vanadium(II)[1]

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Abstract: The complex $VCl_2(py)_4$ was rapidly oxidized by several aralkyl halides, RX, to vanadium(III) and an almost quantitative yield of RR: $2V(II) + 2RX \rightarrow RR + 2V(III) + 2X^-$. No products of the type RH were observed. Only activated halo compounds, *e.g.*, benzyl bromide, were reduced; the reactivity order was RBr > RCl and $CHal_3 > CHal_2 > CHal$. Nonactivated halo compounds, *e.g.*, vinyl halides and alkyl monohalides, were inert. The reactions were first order in oxidant and reductant and were accelerated by electron-withdrawing substituents. For the reduction of benzotrichloride in THF, $\Delta H^{\ddagger} = 17.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.5$ eu. Initial attack on the V(II) complex by the aralkyl halide *via* an outer-sphere mechanism may form a radical which rapidly reacts with a further V(II) yielding an aralkyl vanadium(III) intermediate. This can be rapidly oxidized by another RX to yield the coupled product exclusively. The coupled products are not formed by dimerization of free radicals. Alternatively, an initial inner-sphere attack may produce an aralkyl vanadium(IV) species which is rapidly reduced to the aralkyl vanadium(III) intermediate by a further vanadium(II). Dicyclopentadienylvanadium, which reacted more rapidly with aralkyl halides than did $VCl_2(py)_4$, also yielded coupled products and no RH. Both vanadium compounds reduced *vic*-dihalides to the corresponding olefins.

Alkyl and aralkyl halides, RX, are reduced by many low-valent transition metal compounds, often *via* organometallic intermediates. Mixtures of RH and the coupled compound R–R are commonly formed in proportions depending on the specific halide, metal, ligands, and conditions used; vicinal dihalides are generally dehalogenated to the olefin.

Such reductions by vanadium(II) have been neglected except for reports that dicyclopentadienylvanadium (Cp_2V) reduces benzyl chloride to bibenzyl[2] and carbon tetrachloride to tetrachloroethylene *via* hexachloroethane[3] and that aqueous vanadous salts reduce benzyl chloride to toluene and bibenzyl.[4] Because V(II) differs from Cr(II), the reactions of which have been studied in great detail, in being a weaker reductant, being an electron donor from a t_{2g} rather than an e_g orbital, and being substitutionally inert,[5] we have studied the reactions of organic halides with V(II).

Experimental Section

Materials. $VCl_2(py)_4$ was prepared from VCl_4 by Quarles' method.[6] Vanadous chloride in 90% THF–0.5 *F* HCl was prepared by reduction of VCl_3 with zinc amalgam. Higher concentrations of THF gave only messy black precipitates. Cp_2V[7] was vacuum sublimed. Tetrahydrofuran (THF) was distilled over sodium and redistilled from lithium aluminum hydride under nitrogen before use. 3-Chlorobenzotrichloride (Aldrich) and 3,4-dichlorobenzotrichloride (K and K) were filtered through neutral alumina and fractionated under reduced pressure of nitrogen (bp 51 and 74°, respectively, at 0.15 mm). 4-Chlorobenzotrichloride (Aldrich) was purified as described previously for benzotrichloride.[8] Benzyl bromide (Eastman) was fractionated under nitrogen (bp 133° at 100 mm) and used immediately. 1,3- and 1,4-bis(trichloromethyl)benzenes (Aldrich) were recrystallized from hexane, mp 39 and 114°, respectively. Other preparations were described previously.[8] The compounds were kept anaerobic and anhydrous and their purities checked by vpc and nmr.

Measurements. Because $VCl_2(py)_4$ is rapidly oxidized to vanadium(IV) by oxygen and peroxides, all operations were performed under oxygen- and peroxide-free conditions.

Vanadium valence states were determined polarographically with a dropping mercury electrode.[9] To avoid interference from organic compounds, vanadium solutions were hydrolyzed with 0.2 *N* sulfuric acid and extracted twice with hexane, and the aqueous phase was polarographed immediately.

Kinetic Measurements. Upon oxidation by organic halides, the red $VCl_2(py)_4$ solution in THF forms a pale pink, or in the presence of water pale yellow, V(III) solution (which is rapidly oxidized by air to pale green V(IV)). The reagents were mixed in a thermostated (±0.05°) cell block, and reaction followed at 480 nm. Reactions in benzene, methylene dichloride, and benzonitrile produced insufficient spectral changes for such measurements.

The formation of V^{3+} from VCl_2 in 90% THF–0.5 *F* HCl was followed at 428 nm.

Product yields were measured by gas chromatography as described previously.[8] Controls containing no $VCl_2(py)_4$ were analyzed where necessary. Products were generally identified by comparison with authentic samples and by mass spectroscopy. Products were isolated from some larger scale reactions by extracting twice with equal parts of water and hexane and evaporating the dried hexane layer.

Results

$VCl_2(py)_4$ is oxidized to V(III) by activated organic halides (Table I). It is not oxidized by alkyl mono-

Table I. Reactivities of Organic Halides toward $VCl_2(py)_4$

Compound	Reactivity[a]	Compound	Reactivity[a]
CBr_4	>200	$C_6F_5CH_2Br$	2
Ph_3CBr	200	$PhCHBr_2$	2
Ph_2CHCl	40	CCl_4	1
$PhCCl_3$	40	$2\text{-}BrC_5H_4N$	0.1
$PhCOCl$	40		
$CCl_2{=}CClCCl_3$	5	$PhCH_2Br$	0.1
$CH_2{=}CHCH_2I$	2	$PhCH_2Cl$	0.05
$BrCCl_3$	2	$CH_2{=}CClCH_2Cl$	0.02

[a] Approximate reactivities relative to CCl_4 in THF at 20°.

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Table II. Products from Reductions of Aralkyl Halides by $VCl_2(py)_4$

Oxidant	Solvent	Products	Remarks[a]
$PhCH_2Br$	THF	$(PhCH_2)_2$	See Table III; no PhMe
$PhCH_2Cl$	THF	$(PhCH_2)_2$	No PhMe
Ph_2CHCl	THF, C_6H_6, CH_2Cl_2, or PhCN	$(Ph_2CH)_2$[b]	91% yield isolated; no Ph_2CH_2
$PhCHBr_2$	THF	$(PhCHBr)_2$[c] + *trans*-PhCH=CHPh (3:1)	No *cis*-PhCH=CHPh; no $PhCH_2Br$
$PhCCl_3$[d]	THF, C_6H_6	$(PhCCl_2)_2$	See Table IV; 80% yield isolated; traces of PhCCl=CClPh; no $PhCHCl_2$, $PhCH_2Cl$, or $PhCH_3$
$3\text{-}ClC_6H_4CCl_3$	THF	$(3\text{-}ClC_6H_4CCl_2)_2$[b]	No substituted derivatives of $PhCHCl_2$ or $PhCHCl_2$ or $PhCH_3$
$4\text{-}ClC_6H_4CCl_3$	THF	$(4\text{-}ClC_6H_4CCl_2)_2$[b]	
$3,4\text{-}Cl_2C_6H_3CCl_3$	THF	*e*	
m-$CCl_3C_6H_4CCl_3$	THF	Brown polymer	Infusible up to 300°; mol wt 900–6000[e]
$(PhCCl_2)_2$	THF	PhCCl=CClPh cis:trans (4:1)	High yield; no PhC≡CPh
C_2Cl_6	THF	$CCl_2=CCl_2$	Yield erratic, 26–98%

[a] Yields based on initial $[VCl_2(py)_4]/2$. In all cases $VCl_2(py)_4$ was oxidized to V(III) only. [b] Too involatile to be confirmed by mass spectrometry. [c] Forms no molecular ion at mass no. 340 but instead gives mass spectrum of *trans*-stilbene due to debromination in the spectrometer. [d] Reduction by V^{2+} in 90% THF–0.5 *F* HCl also gave high yields of $(PhCCl_2)_2$ and no benzal chloride, etc. Only V(III) was formed. [e] No product eluted from vpc, consistent with the formation of 3,3′,4,4′-tetrachlorotolane tetrachloride.

halides, vinyl halides, aryl halides, or organic fluorides. Reactivities generally follow the order

$$-CHal_3 \gg -\overset{|}{C}Hal_2 \gg -\overset{|}{\underset{|}{C}}Hal \text{ and } CBr > CCl$$

Product Analysis. The reduction products are summarized in Tables II–IV. Except with the vicinal dihalides, which gave olefins inert to further reduction, only coupled products or their reduction products were formed; in no case were RH-type products detected.

Table III. Yields of Bibenzyl from the Reduction of Benzyl Bromide by $VCl_2(py)_4$ (THF Solvent, Temperature *ca.* 23°)

Initial $10^3[VCl_2(py)_4]$, *M*	Initial $10[PhCH_2Br]$, *M*	$10^3[(PhCH_2)_2]$, *M*, produced	% yield of $(PhCH_2)_2$ (±2%)[a]
9.8	4.93	3.9	80
10.0	3.82	3.9	78
10.2	2.65	4.2	82
10.3	1.66	4.5	88
10.4	0.83	4.3	83
10.5	0.35	4.5	86

[a] Based on initial $[VCl_2(py)_4]/2$. Error limits are standard error of mean coupled product measured.

Table IV. Yields of Tolane Tetrachloride from the Reduction of Benzotrichloride by $VCl_2(py)_4$ (THF Solvent, Initial $[VCl_2(py)_4] = 9.9 \times 10^{-3}$ *M*, Temperature *ca.* 20°)

Initial $10^3[PhCCl_3]$, *M*	$10^3[PhCCl_3]$, *M* consumed[b]	$10^3[(PhCCl_2)_2]$, *M*, produced	% yield[a,c] $(PhCCl_2)_2$ (±3%)
189		4.64	93
122		4.42	89
70	11.3 ± 2.0	4.08	83
46	12.3 ± 1.5	3.69	75
28.2	10.7 ± 0.9	3.37	68
14.1	9.8 ± 0.4	2.99	60

[a] As for Table III. [b] Error limits are standard error of differences of means. [c] Extrapolated yield at infinite benzotrichloride concentration is 5.0×10^{-3} *M*, or 100%.

The solvent had little effect on the products. *sym*-Tetraphenylethane (91%) was isolated from the reduction of benzhydryl chloride in THF; recrystallization from benzene–ethanol gave white crystals, mp 218°, mmp 222° (lit.[10] 215°).

Anal. Calcd for $C_{14}H_{12}$: C, 93.4; H, 6.6. Found: C, 93.4; H, 6.6.

Similarly, benzotrichloride in THF yielded 80% of tolane tetrachloride, recrystallized from benzene–ethanol as white crystals, mp 162°, mmp 164° (lit.[8,10] 162°).

Anal. Calcd for $C_{14}H_{10}Cl_4$: C, 52.5; H, 3.2; Cl, 44.3. Found: C, 52.7; H, 3.2; Cl, 44.4.

Reaction Kinetics. Benzyl halides oxidized $VCl_2(py)_4$ too slowly for convenient kinetic measurement (Table I).

The reduction of benzotrichloride in THF followed eq 1 over at least 2–3 half-lives (correlation coefficients

$$-d[VCl_2(py)_4]/dt = k_2[VCl_2(py)_4][PhCCl_3] \quad (1)$$

>0.9994) (Table V). $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 17.3 kcal mol^{-1} and −3.5 eu, respectively (Table VI). The reaction was much slower in benzene and benzonitrile.

Reduction of benzotrichloride by VCl_2 in 90% THF–0.5 *F* HCl was first order in V^{2+} over about 3 half-lives. The dependence on oxidant was not determined, but if first order would imply $k_2 \simeq 7 \times 10^{-4}$ M^{-1} sec^{-1} at 25°, 400 times slower than reduction by $VCl_2(py)_4$.

Ring-substituted benzotrichlorides also followed eq 1. The ln k_2 values correlate somewhat poorly (correlation coefficient 0.882) with the Hammett σ values[11] (Table VII), ρ being 1.2 (standard error 0.3). Hydroxyl-substituents formed a yellow complex with the V(III) produced which interfered with rate measurements; nitro groups instantaneously oxidize $VCl_2(py)_4$ to V(IV) and V(V).

***vic*-Dichlorides.** The reduction of tolane tetrachloride was extremely slow; after an initial short burst

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Table V. Kinetics of Reduction of Benzotrichloride by $VCl_2(py)_4$ (Temperature 20.1°, THF Solvent)

$10^2[PhCCl_3]$, M	$10^3k'$, $sec^{-1\,a}$	$10k_2$, $M^{-1}\ sec^{-1\,b}$
a. Initial $[VCl_2(py)_4] = 4.9 \times 10^{-4}\ M$		
20.2	25.6	1.27
16.2	21.2	1.31
10.1	13.1	1.30
4.05	5.45	1.34
2.02	2.71	1.34
1.01	1.50	1.48
0.81	1.20	1.48
0.40	0.52	1.30
b. Initial $[VCl_2(py)_4] = 1.45 \times 10^{-4}\ M$		
12.1	17.4	1.44
4.05	5.80	1.43
1.01	1.54	1.52

^{a} Calculated as $k' = d \ln [VCl_2(py)_4]/dt$. ^{b} $k_2 = k'/[PhCCl_3]$. The regression line through the origin gives $k_2 = 0.131\ M^{-1}\ sec^{-1}$ (standard deviation 0.002, correlation coefficient 0.9989). k_2 does not differ significantly (at the 95% confidence level) between the two initial V(II) concentrations used.

Table VI. Activation Parameters for the Oxidation of $VCl_2(py)_4$ by Benzotrichloride (THF Solvent)

T, °C	$10k_2$, M^{-1} $sec^{-1\,a}$	T, °C	$10k_2$, M^{-1} $sec^{-1\,a}$
a. Initial $[VCl_2(py)_4] = 1.89 \times 10^{-4}\ M$			
59.6	47.1	44.8	19.2
55.7	32.0	39.9	8.75
49.2	24.7		
b. Initial $[VCl_2(py)_4] = 3.78 \times 10^{-4}\ M$			
35.0	5.61	15.1	0.796
30.0	3.39	10.0	0.440
25.0	2.14	5.0	0.255
20.1	1.28		

^{a} Activation parameters calculated from the regression line of ln k_2 upon $10^3/T_{abs}$ (°K^{-1}) are $\Delta H^{\ddagger} = 17.3$ kcal mol^{-1}, $S_{\Delta H^{\ddagger}} = 0.38$; $\Delta S^{\ddagger} = -3.5$ eu at 30.5°, $S_{\Delta S^{\ddagger}} = 1.23$; $\Delta G^{\ddagger} = 18.4$ kcal mol^{-1} at 30.5°, $S_{\Delta G^{\ddagger}} = 0.53$; correlation coefficient = 0.9978.

Table VII. Rates of Oxidation of $VCl_2(py)_4$ by Substituted Benzotrichlorides (Temperature 20.0°, THF Solvent)^a

Substituent	$10k_2$, M^{-1} $sec^{-1\,b}$	Std error of $10k_2$	$10k_2$ per $-CCl_3$ group, $M^{-1}\ sec^{-1}$	Hammett σ value
H	1.31	0.02	1.31	0
3-Cl	3.0 (3.0)	0.049 (0.026)	3.0	0.37
3-CCl_3	6.4 (6.3)	0.080 (0.087)	3.2	0.40
4-Cl	3.9	0.022	3.9	0.24
4-CCl_3	9.4 (9.4)	0.18 (0.096)	4.7	0.46
3,4-Cl_2	7.6	0.08	7.6	0.53

^{a} Values in parentheses include those measurements made in systems containing water. ^{b} First-order dependence on V(II) (correlation coefficients >0.999) and halide (correlation coefficients 0.9988 to 0.9999) over at least 2–3 half-lives.

it approximately followed eq 1 over 2 half-lives (Table VIII); k_2 is about $^1/_{215}$ of that for benzotrichloride.

The faster reduction of hexachloroethane also approximately followed eq 1 over 2 half-lives (Table VIII). This reduction is slower than that of benzotrichloride because of a less favorable $\Delta S^{\ddagger}$ (significant at the 2.5% level).

Table VIII. Rate of Reduction of *vic*-Dihalides by $VCl_2(py)_4$ (Initial $[VCl_2(py)_4] = 3.05 \times 10^{-4}\ M$, THF Solvent)

Temp, °C	10^2[dihalide], M	$10^4k'$, sec^{-1}	10^3k_2, M^{-1} $sec^{-1\,a}$
(a) Tolane Tetrachloride			
44.6	1.12	0.98	8.8
44.6	4.46	4.0	9.0
44.6	22.3	20.1	9.0
			Mean 8.9
(b) Hexachloroethane			
45.0	13.7	143	10.4
45.0	7.2	82	11.3
35.0	13.7	81	5.9
35.0	9.7	60	6.3
35.0	7.2	46	6.3
25.0	7.2	23.4	3.2
16.0	16.1	14.5	0.90
16.0	9.7	7.7	0.80
6.0	9.7	2.56	0.265

^{a} $\Delta H^{\ddagger} = 16.4$ kcal mol^{-1}, $S_{\Delta H^{\ddagger}} = 0.094$; $\Delta S^{\ddagger} = -11$ eu at 25.5°, $S_{S\Delta^{\ddagger}} = 3.1$; $\Delta G^{\ddagger} = 19.7$ kcal mol^{-1} at 25.5°, $S_{\Delta G^{\ddagger}} = 1.3$; correlation coefficient = 0.989.

Effect of Proton Acids and Free Radical Traps. No intermediates were detected spectrally in the oxidations of $VCl_2(py)_4$. No transient peak developed and as the $VCl_2(py)_4$ peak (480 nm in THF, 535 nm in benzene) disappeared without shifting only that for V(III) appeared.

Proton acids and free-radical traps were added to try to trap organo vanadium or free-radical intermediates, respectively. Concentrations of water up to five times the initial $VCl_2(py)_4$ had little effect on the $VCl_2(py)_4$ spectrum, reaction rate (Table VII), rate law, or reaction products. High yields of tolane tetrachloride and no traces of benzal chloride, benzyl chloride, or toluene were produced. (Aqueous vanadous chloride also reduced benzotrichloride to tolane tetrachloride.) However, the final color changed from pale pink to pale yellow because of complexing of the substitutionally labile V(III).[5] Likewise, excess phenol caused no pronounced alteration in reaction rate or yield of tolane tetrachloride, and no benzal chloride, benzyl chloride, or toluene was produced in its presence.

Addition of excess of the free-radical trap cyclo-1,4-hexadiene also had no effect on the reaction products.

Reduction by Cp_2V. Cp_2V in ether reduces benzyl chloride to bibenzyl.[2] In THF or hexane it reacts with aralkyl halides faster than $VCl_2(py)_4$ does, but also yields only the coupled products, or compounds derived therefrom (Table IX). No RH-type products were observed.

Table IX. Reactivity of Vanadocene with Organic Halides in THF

Oxidant	Products^{a,b}
$PhCCl_3$	$PhCCl_2CCl_2Ph$ + *ca.* 20% *cis*- and *trans*-$PhCCl{=}CClPh$; no $PhCHCl_2$, $PhCH_2Cl$, or $PhCH_3$
Ph_2CHCl	$Ph_2CHCHPh_2$; no Ph_2CH_2
$PhCHBr_2$	$PhCHBrCHBrPh$ + *trans*-$PhCH{=}CHPh$ + *cis*-$PhCH{=}CHPh$ (2.5:8:1)
$PhCH_2Br$	$PhCH_2CH_2Ph$; no $PhCH_3$

^{a} Nonactivated halides, *e.g.*, alkyl monohalides, aryl halides, and benzotrifluoride, do not react. ^{b} Cp_2V forms a blue tetrahydrofuran solution. These reactions show marked color changes and sometimes deposit green crystals. Reactions in hexane are similar but form messy precipitates.

Table X. Activation Parameters for the Reduction of Organic Halides by Transition Metal Compounds

Halide	Reductant	Medium	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Ref
$PhCH_2Cl$	Cr^{2+} aq	71.5% EtOH	14.0	−14.3	13
trans-1,2-Dibromocyclohexane	Cr^{2+} aq	88% DMF	11.2	−20.8	17
cis-1,2-Dibromocyclohexane	Cr^{2+} aq	88% DMF	13.2	−24.2	17
c-$C_6H_{11}Br$	Cr^{2+} aq	88% DMF	14.4	−27.2	17
p-$BrCH_2C_6H_4COO^-$	$Co(CN)_5{}^{3-}$	$NaClO_4$ aq	3.8	−36	27
$(^-OOCCHBr)_2$ *meso*-	$Co(CN)_5{}^{3-}$	$NaClO_4$ aq	5.0	−33	27
dl-		$NaClO_4$ aq	6.2	−34	27
$PhCH_2Br$	$Co^{II}(DMH)_2PPh_3$	PhH	10.1	−32	22
$PhCH_2Br$	$Co^{II}(DMH)_2py$	PhH	9.9	−29	22
$PhCH_2Cl$	Bu_3P–cobaloxime(I)	MeOH–H_2O	7	−25	29
CH_3I	$Ir(^I)CO[PPh_3]_2Cl$	C_6H_6	5.6	−51	*a*
		DMF	16.4	−10	*a*
$CHCl_2Br$	$CoCp_2$	EtOH	13.6	−16.7	*20*
CCl_4	$CoCp_2$	EtOH	12.8	−18.7	20
$(PhCHBr)_2$ *meso*-	$SnCl_2$	DMF	15.5	−28	*b*
dl-			19.3	−21	*b*

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Discussion

The oxidations of $VCl_2(py)_4$ by aralkyl halides all selectively form coupled compounds, R–R, with the complete absence of RH-type products (Table II). Although coupled products are frequently formed from reduction of organic halides by transition metal compounds, they are often obtained together with RH-type products. Thus Cr(II) reduces benzyl halides to bibenzyl and toluene in proportions depending on the conditions,[4,12,13] benzyl chloride to toluene in DMF–H_2O but to stilbene in EtOH–H_2O,[14] and benzotrichloride to toluene only by a route not involving benzal or benzyl chlorides.[14] Fe^{2+} will not reduce benzyl chloride but generally couples polyhalogeno compounds, while Cu(I) reduces benzyl chloride to toluene and bibenzyl in proportions depending on added complexing agents.[15,16] Tables III and IV indicate the stoichiometry

$$2\mathrm{P.X} + 2\mathrm{V(II)} \longrightarrow \mathrm{R{-}R} + 2\mathrm{V(III)} + 2\mathrm{X}^- \qquad (2)$$

The origin of the decrease in tolane tetrachloride yield with decreasing initial benzotrichloride concentration (Table IV) is not known, but secondary reduction of tolane tetrachloride is too slow to account for it (Table VIII). Reductions by Cp_2V follow the analogous stoichiometry.[2]

The dechlorination of *vic*-dihalides by $VCl_2(py)_4$ is similar to reaction with Cr(II)[17] and Cu(I).[15,16]

$\Delta S^{\ddagger}$ for the reduction of benzotrichloride (−3.5 eu) is much less unfavorable than those for similar reactions of other reductants which are generally either substitutionally labile or have a vacant coordination site (Table X) and is offset by a relatively high $\Delta H^{\ddagger}$. Although activation entropies are not always very diagnostic, this suggests an outer-sphere reaction. An outer-sphere reaction may be favored here since unlike Cr(II), which probably reacts by an inner-sphere process,[13,18] V(II) is substitutionally inert and direct electron transfer from a V(II) t_{2g} orbital to an antibonding oxidant orbital could occur

$$\mathrm{RX} + \mathrm{V(II)} \longrightarrow \mathrm{R}\cdot + \mathrm{V(III)} + \mathrm{X}^- \qquad (3)$$

This outer-sphere route was proposed for the reduction of nitrobenzyl halides by bis(*N*-methyl-*N′*-salicylidene)ethylenediaminocobalt(II)[19] and of benzyl chloride by cobaltocene.[20] It is consistent with the marked acceleration by electron-withdrawing substituents (Table VII) and the reactivity order $CHal_3 > CHal_2 > CHal$. Similar acceleration by electron-withdrawing substituents is found when benzyl halides are reduced polarographically ($\rho = 1.45$),[21] by $Co(DMH)PPh_3$ ($\rho = 1.48$),[22] by $Co(CN)_5{}^{3-}$,[23] and by cobaltocene.[20] In contrast, reduction by Cr(II) is little affected by substituents.[13]

In added support for an outer-sphere mechanism, the reactivity ratio k_{Br}/k_{Cl} for reductions by $VCl_2(py)_4$ is about 2. This is similar to values of 2–6 for outer-sphere reductions of nitrobenzyl halides by Co(II)[19,24] and 2–3 for outer-sphere reduction of $Ru(NH_3)_5Hal^{2+}$ and $Co(NH_3)_5Hal^{2+}$ by V^{2+}.[25,26] In contrast, k_{Br}/k_{Cl} is about 10^2 for Cr(II)[13,18] and 10^3–10^4 for five-coordinate Co(II)[22–24,27,28] for inner-sphere reductions of organic halides.

An inner-sphere mechanism in which the aralkyl halide complexes the $VCl_2(py)_4$, followed by halogen transfer, cannot be ruled out, however. As these reactions are relatively slow, the substitution of $VCl_2(py)_4$

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may be fast enough. Halogen bridged intermediates have been proposed in reductions of aralkyl halides by Fe(II),[15] Cu(I),[15] Cr(II),[12,13] and five-coordinate Co(II),[24] and are more likely for a d^3 ion than direct SN2 attack on the α carbon.[24,29] As V(III) complexes are substitutionally labile, one cannot distinguish between an inner- or outer-sphere route from the fate of the halide liberated.

However step 3 occurs, it probably forms a radical which reacts rapidly with another V(II) to form an organovanadium intermediate.

$$\mathrm{R}\cdot + \mathrm{V(II)} \longrightarrow [\mathrm{R{-}V(III)}] \qquad (4)$$

Thus, radicals are formed in reductions of halo compounds by Cr(II),[14,18] $\mathrm{Co(CN)_5}^{3-}$,[24] and Cu(I).[30] Our failure to trap radicals with phenol or cyclo-1,4-hexadiene is not evidence against radical formation, since they may be stabilized by association with the V(III) species, and step 4 may be very rapid since V(II) is paramagnetic d^3. Reactions of alkyl radicals with $\mathrm{Cr^{II}en}$[18] and $\mathrm{Cr(H_2O)_6}^{2+}$ [31] have rate constants of 3×10^7 to 3×10^8 M^{-1} sec^{-1}.

Formation of coupled products by radical dimerization is unlikely. A stationary-state calculation, taking rate constants of 4×10^9 M^{-1} sec^{-1} for benzyl radical dimerization[32] and 10^7 M^{-1} sec^{-1} for step 4,[18,31] indicates that dimerization is 10^5–10^6 times slower than step 4. The rapidity of step 4 likewise explains the complete absence of RH-type products. THF is probably not very active toward radicals; thus the rate constant for methyl radical attack on dioxane is only 7×10^3 M^{-1} sec^{-1} at 110°.[33] The hydrogen in alkanes produced by $\mathrm{Cr^{II}en}$ reduction of organic halides arises exclusively from protolysis of an intermediate alkyl chromium complex and not by hydrogen abstraction from the DMF solvent.[18]

Routes not involving radicals are possible if there is oxidative addition of the aralkyl halide to the vanadium[24]

$$\mathrm{RX} + \mathrm{VL_6} \longrightarrow \mathrm{RVL_4X} + 2\mathrm{L} \qquad (5)$$

Since V(II) is (t_{2g}),[3] overlap with the R group may then favor its capture rather than its expulsion as a radical. The organovanadium(IV) intermediate can then be rapidly reduced

$$\mathrm{RVL_4X} + \mathrm{V(II)} \longrightarrow [\mathrm{R{-}V(III)}] + \mathrm{V(III)} \qquad (6)$$

Whichever path be followed, an organo-vanadium(III) intermediate is involved. Unlike the cases of reductions by Cr(II)[12,18,34] and Co(II),[22,24] this was not detected spectrally or kinetically or trapped by proton acids. However, acid cleavage to alkanes is fairly slow[12,35] so that this is not evidence against organo vanadium intermediates. The resemblance of $\mathrm{VCl_2(py)_4}$ reductions to those by $\mathrm{Cp_2V}$—which involve a $\mathrm{Cp_2VR}$ intermediate—supports the formation of such an intermediate.

The specific formation of coupled products probably results from

$$[\mathrm{R{-}V(III)}] + \mathrm{RX} \longrightarrow \mathrm{R_2} + \mathrm{V(III)} + \mathrm{X^-} \qquad (7)$$

Thus in Cr(II) reduction of benzyl halides the benzyl chromium(III) intermediate reacts with benzyl halide to form bibenzyl while reaction between two benzylchromium ions is much slower.[12] As V(III) is substitution labile,[5] reaction 7 may involve rapid addition to form $[\mathrm{R_2V^V}]$ which then rapidly decomposes to $\mathrm{R_2}$ and V(III). Benzylchromium(III) and alkylcobalt(III) complexes are substitution inert, so their reactions with alkyl halide are much slower, allowing them to be detected.

Compounds containing vanadium–carbon σ bonds are unusual. Only a few are known in valencies (II),[36] (IV),[37-39] and (V).[39] Apart from a few $\mathrm{Cp_2VR}$[38,40] compounds, no V(III) compounds containing a vanadium–carbon σ bond are known. The likely formation of σ-bonded aralkyl vanadium(III) intermediates in the reduction of aralkyl halides by $\mathrm{VCl_2(py)_4}$ is of considerable interest, especially when it is considered that industrially important processes using vanadium catalysts, *e.g.*, the Ziegler–Natta polymerization of olefins, probably involve σ-bonded alkylated V(III) intermediates.

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