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The Significance of the Absence of Evidence of Chelation in the Functioning of Salicylate Ion as a Bridging Ligand for Electron Transfer between Ruthenium(III) and Titanium(III)

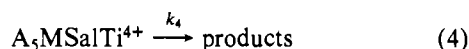
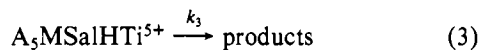
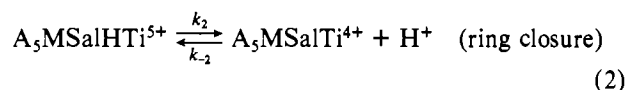
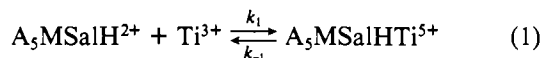
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Martin and Gould¹ have shown that the acid dependence of the rate of reaction between Ti(III) and several salicylate complexes of Co(III) indicates that chelation of Ti(III) to the bridging ligand occurs prior to electron transfer (ET). We now report data that demonstrate that a different mechanism operates in the reduction of a corresponding complex of ruthenium(III).

(Salicylate)pentaammineruthenium(III) perchlorate was prepared with use of the method of Stritar and Taube.² Anal. Calcd for $[\text{Ru}(\text{NH}_3)_5\text{C}_7\text{H}_6\text{O}_3]\text{ClO}_4$: Ru, 19.3, C, 16.1; N, 13.4; H, 3.8. Found: Ru, 19.1; C, 15.9; N, 13.6; H, 3.7.^{3,4} The UV-visible spectrum showed peaks at 410 ($\epsilon = 245 \text{ M}^{-1} \text{ cm}^{-1}$) and 295 nm ($\epsilon = 6030$). The complex gave a formal redox potential of 55 mV vs. NHE (cyclical voltammetry at pH 1.5 in 1 M LiCl). Reduction⁵ of the complex by Ti(III) gave a second-order rate constant of $(6.3 \pm 0.1) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ independent of $[\text{H}^+]$ over the range tested $[\text{H}^+]$ (0.4–0.12 M in 1 M LiCl at 25.0 °C). This acid-independent second-order rate constant is similar to the value determined⁵ for $\text{Ru}(\text{NH}_3)_5\text{OOCCH}_3^{2+}$ ($7.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$) and for⁶ $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+}$ ($8.1 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$).

The results can be discussed on the basis of the mechanism



When $\text{M} = \text{Co}$ the data indicate that one of the factors determining the rate is a competition between ET within a deprotonated and chelated intermediate (reaction 4) and proton-assisted decomposition of that intermediate (the reverse of reaction 2). no such complication occurs when $\text{M} = \text{Ru}$, indicating a fundamental change in mechanism.⁶

The measured reduction potential and data on related systems⁸ leads to the estimate $k_{11} = 3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the electron-exchange rate constant of the Ru(III)–Ru(II) couple of interest. Combining this estimate with the estimate of the $\text{Ti}^{4+}/\text{Ti}^{3+}$ electron-exchange rate constant given by Brunschwig and Sutin⁹ leads to a predicted outer-sphere redox rate constant of $k_{12} \approx 0.6 \text{ M}^{-1} \text{ s}^{-1}$ for the present reaction. taking a value of 0.01 M^{-1} for the ion-pair (or encounter) complex

formation constant appropriate to that reaction yields a first-order rate constant of $\sim 60 \text{ s}^{-1}$ for outer-sphere Ru(III)–Ti(III) ET.

Diebler¹⁰ has found that the rate constant for substitution of acetate onto (acetato)titanium(III) is $k_1 \approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Using a value of 10^0 M^{-1} for the ion-pair formation constant for this process leads to a value of 10^7 s^{-1} for the first-order rate constant for water loss from Ti(III). The labilizing effect of a carboxyl group which is already coordinated to Ru(III) would be expected to be less than that of acetate ion.¹¹ This leads to the estimate of $k_2 \approx 10^5 \text{ s}^{-1}$.

The lack of a $[\text{H}^+]$ dependence in the $\text{M} = \text{Ru}$ case implies either $k_3 > k_2$ or $k_4 > k_{-2}[\text{H}^+]$. On the basis of equilibrium measurements on the Fe(III) complex,¹² it appears that $k_2 \approx k_{-2}[\text{H}^+]$, so that on either basis $k_{\text{ET}} (=k_3 \text{ or } k_4) > 10^5 \text{ s}^{-1}$. The divergence between $K > 10^5 \text{ s}^{-1}$ (inner-sphere ET) and $K \approx 60 \text{ s}^{-1}$ (outer-sphere ET) is consistent with greater cross-bridge electronic interaction in the inner-sphere case. The divergence between the results with $\text{M} = \text{Co}$ and $\text{M} = \text{Ru}$ is consistent with the expectation that cross-bridge electronic interaction through the π system of the carboxylate bridge is greater in the $t_{2g}-t_{2g}$ case (Ru(III)–Ti(III)) than in the e_g-t_{2g} case (Co(III)–Ti(III)).

Acknowledgment. R.N.B. is grateful to the University of Dacca, Bangladesh, for a study leave.

Registry No. $[\text{Ru}(\text{NH}_3)_5\text{C}_7\text{H}_6\text{O}_3]\text{ClO}_4$, 77744-87-7; Ti^{3+} , 22541-75-9.

(10) Diebler, H., private communication.

(11) We are grateful to Dr. H. Diebler for calling our attention to this.

(12) Park, M. V. *J. Chem. Soc. A* 1966, 816. Quoted in: Martell, A. E.; et al. "Stability Constants, Supplement 1"; The Chemical Society: London, 1971; p 25.

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Ammonolysis of Bis(trifluoromethyl)phosphine: A Source of New Chiral Phosphines

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A paper presented at a recent meeting¹ described some new products obtained by the reaction of $(\text{CF}_3)_2\text{PH}$ with trimethylamine: bis(phosphino)methanes, $\text{R}(\text{CF}_3)_2\text{PP}(\text{CF}_3)_2$ compounds (where R is CHF_2 , CH_2F , or CH_3), and other phosphines derived from their P–P bond cleavage reactions. Of the whole list, the compounds most difficult to obtain in good yields and purity were $\text{CHF}_2(\text{CF}_3)_2\text{P}(\text{CF}_3)_2$ and $\text{CH}_2\text{F}(\text{CF}_3)_2\text{P}(\text{CF}_3)_2$; they were identified only by their NMR spectra and further chemistry. Thus it seemed useful to repeat the action of ammonia on $(\text{CF}_3)_2\text{PH}$, which had been reported to lead through CF_3PCF_2 to $\text{CHF}_2(\text{CF}_3)_2\text{PNH}_2$, convertible to $\text{CHF}_2(\text{CF}_3)_2\text{P}(\text{CF}_3)_2$ by action of HCl .² Table I presents the stoichiometry of three such experiments.

For experiment 1 the reactants, in a 40-mL stopcocked tube, were warmed from -130 to -110 °C during 60 min, then quickly to -70 °C, and to -50 °C in 5 min. The volatiles were

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Table I. Stoichiometry (mmol) of $(CF_3)_2PH-NH_3$ Reactions, with Conversion of Amides to Chlorides

	expt		
	1	2	3
$(CF_3)_2PH$	2.766	4.506	5.264
NH_3 in	6.870	16.641	16.998
NH_3	1.338	8.878	6.067
NH_3 consumed	5.532	7.763	10.931
HCl in	5.577	7.883	11.002
HCl recovered	1.704	0.071	0.834
HCl consumed	3.873	7.812	10.168
$(CF_3)_2PCL$	0.642	0.906	1.767
$CHF_2(CF_3)PCL$	0.339	1.909	1.347
$CH_2F(CF_3)PCL$	0.727	0.680	0.589
$(CF_3)_2PCH_2P(CF_3)Cl$	<i>a</i>	0.112	0.076
$HN[P(CF_3)_2]_2$	<i>a</i>	0.214	0.112

^a In experiment 1, these components were seen but not measured separately. They accounted for about 7% of the P in $(CF_3)_2PH$. As mentioned before, $HN[P(CF_3)_2]_2$ resists HCl.³

brought into the Stock-type high-vacuum manifold as the reaction tube was warmed from -40 to 50 °C. The excess ammonia was removed by passage through a high-vacuum U-trap at -78 °C and measured. Full recovery of the ammonia required several repetitions of this fractional condensation. The main middle fraction then showed NMR spectra interpretable in terms of major yields of $(CF_3)_2PNH_2$ and $CH_2F(CF_3)PNH_2$, with considerably less $CHF_2(CF_3)PNH_2$. Then the whole volatile product was treated with HCl in excess, first at low temperatures. The new product mixture was resolved by means of a small high-vacuum reflux column, and the components were separately identified by their NMR spectra.

For experiment 2, the reactants in a 40-mL sealed tube were warmed rapidly to -85 °C and then to 0 °C in 45 min. The products were treated with HCl as before. The far higher yield of $CHF_2(CF_3)PCL$ would correspond to conditions closer to those of the original experiments.²

For experiment 3, the reactants in a 50-mL sealed tube were warmed rapidly from -196 to -78 °C (5 s), then to 0 °C (15 s), and to 25 °C (10 s). Again, the results suggest that secondary processes occurred less extensively than in a slow, low-temperature reaction. However, conditions leading exclusively to $CHF_2(CF_3)PNH_2$ and $CHF_2(CF_3)PCL$ were not found. It is noted that equimolar $(CF_3)_2PCL$ and $CH_2F(CF_3)PCL$ would give the same analysis and average molecular weight as pure $CHF_2(CF_3)PCL$ but a higher yield of HCF_3 by basic hydrolysis (equally true for the amides).

Even a small yield of $HN[P(CF_3)_2]_2$ here is interesting because its synthesis from $H_2NP(CF_3)_2$ requires a special method.³ The compound $(CF_3)_2PCH_2P(CF_3)Cl$ was reported;¹ its formation here could be explained by more than one complex series of processes.

The least volatile fractions showed NMR spectra indicating low yields of other polyphosphines, not yet identified. In experiment 3 they represented about 5% of the $(CF_3)_2PH$.

NMR spectra were recorded by the Varian XL100-FT instrument, with δ_H measured downfield from Me_4Si , δ_F upfield from Cl_3CF , and δ_P positive upfield from H_3PO_4 , in ppm. The coupling constants πJ , in Hz, have multiplicity indicated by *n*. Infrared frequencies, recorded by the Beckman IR20A instrument, are given in cm^{-1} with relative intensities in parentheses.

N-P Compounds. The ^{19}F and 1H NMR spectra for the initial product mixture from experiment 1 clearly identified the main components. Hydrogen-bond interactions might have affected the parameters, but probably not significantly, for the ^{19}F spectrum of $HN[P(CF_3)_2]_2$ agreed well with a pure

Table II. NMR Parameters of CHF_2 Phosphines

	$CHF_2(CF_3)PNH_2$	$CHF_2(CF_3)PCL$	$CHF_2(CF_3)PH^a$
Proton			
δ	5.91	6.0	6.2
${}_2J_{HCF}$, Hz	50.25	51.3	51
${}_2J_{HCP}$, Hz	22.7	9.2	9.6
Fluorine			
$\delta(CF_3)$	66.71	63.4	49
${}_2J_{FCP}$, Hz	73.2	75.2	58
${}_3J_{FCPCF}$, Hz	7.33	6.98	6.5
$\delta(CHF_2)^b$	128.2, 131.0	119.0, 127.4	113.7, 115.0
${}_2J_{FCP}$, Hz	125.2, 89.7	131.2, 141.8	116.5, 133.6
${}_2J_{FCH}$, Hz	49.8, 50.7	50.86, 51.72	50.89, 51.01
${}_4J_{FCPCF}$, Hz	7.66, 7.03	7.41, 6.63	6.74, 6.31
${}_2J_{FCF}$, Hz	332	346	339
I_O/I_i	0.12	0.43	0.034
Phosphorus			
δ		-43	56
${}_2J_{PCF}$, Hz		131, 139 ^c	118
${}_4J_{PCF}$, Hz		75	131

^a δ_{HP} 3.8, ${}_2J_{HP} = {}_2J_{PH} = 213$ Hz, ${}_2J_{HPCF} = {}_2J_{FCPH} = 15.04$ or $20.5B$ Hz, ${}_4J_{HPCF} = {}_4J_{FCPH} = 10.77$ Hz, ${}_2J_{HPCH} = {}_2J_{HCPH} = 2.56$ Hz. ^b Where two entries are given, the parameters are for F_A and F_B , respectively. The intensity ratios (I_O/I_i) of outer to inner clusters came from the AB calculations and agreed with observation. ^c Different samples.

Table III. NMR Parameters of CH_2F Phosphines

	$CH_2F(CF_3)PNH_2$	$CH_2F(CF_3)PCL$	$CH_2F(CF_3)PH^a$
Proton			
δ	4.6	4.9	4.8
${}_2J_{HCF}$, Hz	48.3	47.4	48.0
${}_2J_{HCP}$, Hz	10.4	12.0	7.8
Fluorine			
$\delta(CF_3)$	66.96	63.8	50.5
${}_2J_{FCP}$, Hz	71.8	74.4	59.7
${}_2J_{FCPCF}$, Hz	6.42	6.62	4.5
$\delta(CH_2F)$	247	239	226
${}_2J_{FCP}$, Hz	90	117	98
${}_3J_{FCH}$, Hz	48.2	47.4	48.0
${}_4J_{FCPCF}$, Hz	6.44	6.61	4.40
Phosphorus			
δ		58	54
${}_2J_{PCF}$, Hz		118	99
${}_4J_{PCF}$, Hz		75	59
${}_3J_{PCH}$, Hz		12.1	7.8

^a δ_{HP} 3.9, ${}_2J_{HP} = {}_2J_{PH} = 224$ Hz, ${}_2J_{HPCF} = {}_2J_{FCPH} = 31.0$ Hz, ${}_4J_{HPCF} = {}_4J_{FCPH} = 10.8$ Hz, ${}_3J_{HPCH} = {}_2J_{HCPH} = 4.75$ Hz. No AB pattern could be recognized for any of the CH_2 groups.

sample: a second-order pattern at δ 65.6, of appearance just like $S[P(CF_3)_2]_2$,⁴ with mutually symmetrical peaks separated by 90.4, 53.0, 37.4, and 14.0 s^{-1} . The ^{19}F spectrum for $(C-F)_2PNH_2$ was interlaced with the other PNH_2 compounds but still could be sorted out: δ_F 66.87, with ${}_2J_{FCP} = 81.1$. Tables II and III give the parameters for $CHF_2(CF_3)PNH_2$ and $CH_2F(CF_3)PNH_2$. The NH_2 group protons showed only one broad peak near δ 3.

The vapor pressures of the mixture varied from 35 to 10 mm at 0 °C as successive fractions were taken off.

Chlorophosphines. The most volatile product of the HCl reaction was identified as $(CF_3)_2PCL$ by its ^{19}F NMR spectrum:⁵ δ 62 and ${}_2J_{FCP} = 85$. Tables II and III show the NMR data for the other chlorophosphines.

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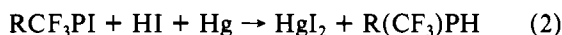
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For nearly pure $\text{CHF}_2(\text{CF}_3)\text{PCl}$, the vapor-phase molecular weight was 186.9 (calcd 186.5). Its volatility (10.7 mm at -45°C , 45.6 mm at -22.6°C , and 150 mm at 0°C) is described by $\log P = 5.538 + 1.75 \log T - 0.005T - 1710/T$ (bp 40°C , Trouton constant 21.2 eu). Its easily observable infrared peaks (with relative intensities) are at 2950 (0.14, wide), 1333 (0.6), 1294 (14), 1213 (11), 1158 (57), 1088 (35), 1023 (26), 982 sh (3), 956 sh (2), 740 (1.4), 550 (3.0), 480 (0.9), 445 (1.6), and 420 cm^{-1} (1.3).

The volatility of $\text{CH}_2\text{F}(\text{CF}_3)\text{PCl}$ (15.7 mm at -22.6°C or 61 mm at 0°C) suggests $\log P = 6.729 + 1.75 \log T - 0.0065T - 2030/T$ (bp 60°C , Trouton constant 21.4 eu). Infrared data: 1430 (0.33), 1380 (0.15), 1309 (0.9), 1260 (0.8), 1169 (19), 1153 (27), 1090 (10), 1034 (10) 922 (0.4), 850 (0.45), 768-720 (0.2), 703 (0.44), 545 (1.6), 518 (1.6), 448 (0.9), 418 cm^{-1} (0.8).

The bis(phosphino)methane $(\text{CF}_3)_2\text{PCH}_2\text{P}(\text{CF}_3)\text{Cl}$ will be more fully described in another paper. Its unusual geminal- CF_3 NMR spectrum left no doubt of its presence. A number of other minor byproducts of the HCl-aminophosphine reaction (with complicated ^{19}F NMR spectra near δ 50) were not identified.

P-H Phosphines. The reaction series



can be completed by three additions of excess HI to the rotatable reaction tube; in the one-run process, the conversion is only 75-80% because the direct removal of HI by Hg intervenes. The yield of HCl may be only half of the calculated value; then Hg_2Cl_2 would account for the rest of the chloride. Reaction 2 was shown in separate experiments to be fully as quantitative as the prototype process with $(\text{CF}_3)_2\text{PI}$.⁶

Tables II and III show the NMR data for both RCF_3PH compounds. Further work with $\text{CHF}_2(\text{CF}_3)\text{PH}$ showed interesting variations which are being studied further by Dr. L. D. Field, a recent member of our Hydrocarbon Institute. For example, ${}_2J_{\text{FCP}}$ for F_A (the downfield member of the AB pattern) varies from 126 Hz in the neat sample at -30°C to 112 Hz in DCCl_3 at 30°C , and similarly ${}_2J_{\text{FCPH}}$ varies from 17.4 to 13.6 Hz; but for F_B these parameters remain nearly constant—and so do all other parameters not relating to F_A and the PH proton. It might be suggested that F_A and the PH proton have a rubbing contact, with some electrostatic attraction. The effect of this would diminish with dilution and

rise of temperature. The concept is justified by the expected bond distances and angles and van der Waals radii; but it is not a final conclusion.

For the purification of $\text{CHF}_2(\text{CF}_3)\text{PH}$ it was considered that the almost equally volatile $\text{CH}_3(\text{CF}_3)\text{PH}$ could be a minor impurity. This could be removed by forming the BH_3 complex, which is not appreciably volatile at -78°C .⁷ Then the 98% pure sample had mol wt 151 (calcd 152), and its volatility (6.3 mm at -63.7°C , 25.8 mm at -45.3°C , and 102.6 mm at -22.7°C) suggested the equation $\log P = 6.000 + 1.75 \log T - 0.006T - 1674/T$ (bp 22°C , Trouton constant 21.3 eu). The significant infrared frequencies are 2967 (0.6), 2335 (0.4), 1404 (0.3), 1308 (4), 1262 (1.6), 1163 (24), 1149 (26), 1092 sh (7), 1070 (1.1), 913 (2.1), 903 (1.8), 855 (3), 824 (2.7) 758 (0.5), 750 (0.5), 720 (0.6), 591 (0.3), 524 (0.8), 445 (1.8), and 360 cm^{-1} (0.2).

For pure $\text{CH}_2\text{F}(\text{CF}_3)\text{PH}$, mol wt = 134, as calculated. Its volatility (3.6 mm at -51.8°C , 15.0 mm at -32.7°C , 28.7 mm at -22.6°C , and 103 mm at 0°C) implies $\log P = 5.756 + 1.75 \log T - 0.005T - 1814/T$ (bp 47°C , Trouton constant 21.3 eu). Its infrared frequencies included fundamentals scarcely stronger than some overtones or combinations; hence all peaks easily observable at 82 mm pressure with path 113 mm are listed: 2925 (0.29), 2825 (0.05), 2590 (0.22), 2313 (0.22), 2265 (0.18, wide), 2064 (0.05), 1978 (0.04), 1928 (0.02), 1876 (0.07), 1750-1550 (0.07), 1438 (0.29), 1315 (0.9), 1260 (0.8), 1179 (15), 1142 (39), 923 (0.8), 876 (0.45), 830 (3.4), 800 sh (0.7), 742 (0.8), 644 (0.09), 555 (0.09), 520 (0.17), 475 (0.07), 410 (0.37), 360 cm^{-1} (0.35).

The NMR parameters of $\text{CH}_2\text{F}(\text{CF}_3)\text{PH}$ did not vary appreciably with dilution.

Significance. The new chiral phosphines are probable precursors of numerous ligands suitable for the study of electronic effects in transition-element complexes. The P-H phosphines also could be used for making $(\text{RCF}_3\text{PBH}_2)_3$ ring compounds offering a wide range of subtly variant properties.

Acknowledgment. Thanks are due to Drs. L. D. Field and K. L. Servis for advice about NMR spectra and to Dr. H. Goldwhite for further information about his earlier publication.²

Registry No. $(\text{CF}_3)_2\text{PH}$, 460-96-8; $(\text{CF}_3)_2\text{PCl}$, 650-52-2; $\text{CHF}_2(\text{CF}_3)\text{PCl}$, 4669-82-3; $\text{CH}_2\text{F}(\text{CF}_3)\text{PCl}$, 77846-29-8; $(\text{CF}_3)_2\text{PCH}_2\text{P}(\text{CF}_3)\text{Cl}$, 77846-30-1; $\text{HN}[\text{P}(\text{CF}_3)_2]_2$, 2349-17-9; $\text{CHF}_2(\text{CF}_3)\text{PNH}_2$, 4669-83-4; $\text{CH}_2\text{F}(\text{CF}_3)\text{PNH}_2$, 77846-31-2; $\text{CHF}_2(\text{CF}_3)\text{PH}$, 77846-32-3; $\text{CH}_2\text{F}(\text{CF}_3)\text{PH}$, 77846-33-4.

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Correspondence

Hydrogen Migration Mechanism for Ligand Substitution Reactions in Metal Carbonyl Hydrides

Sir:

It has been known for some time that certain transition-metal carbonyl hydrides are unusually labile in ligand substitution processes.¹ For example, $\text{HCo}(\text{CO})_4$ is much more reactive than other $\text{XCo}(\text{CO})_4$ molecules.² $\text{HMn}(\text{CO})_5$ is considerably more reactive than similar $\text{XMn}(\text{CO})_5$ molecules.³ The protonated forms of iron pentacarbonyl and

$\text{Fe}(\text{CO})_4\text{PPh}_3$ are much more labile than the parent molecules.⁴ Even the anion $\text{HFe}(\text{CO})_4^-$ undergoes ligand exchange far more rapidly than $\text{Fe}(\text{CO})_5$ does and also much more rapidly than $\text{CH}_3\text{COFe}(\text{CO})_4^-$.⁵ The anions $\text{Co}(\text{CO})_4^-$ and $\text{Fe}(\text{CO})_4^{2-}$ are quite inert.

A mechanism explaining this unusual lability (Scheme I) was offered involving a ligand migration of hydrogen to a

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