The oxidative dehydrogenation of coordinated ligands is seen generally to produce only conjugated imines. Although different metal ions may involve different mechanisms for dehydrogenation, the buildup of conjugated systems can provide a low-energy pathway for an intramolecular oxidation. Future work in progress involves a study of the oxidative dehydrogenation of cobalt(II) complexes of 1,11-bis(2-pyridyl)-2,6,10-triazaundecane and 2-(aminomethyl)pyridine, with the use of fast-atom-bombardment mass spectra as well as the techniques described above.

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Registry No. $[(Co(PYDIEN))_2O_2]Br_4$, 93983-48-3; chloro(1,9-bis-(2-pyridyl)-2,5,8-triazanona-1,8-diene)cobalt(III) perchlorate, 93894-83-8; chloro(1,9-bis(2-pyridyl)-2,5,8-triazanona-1,8-diene)cobalt(III) chloride, 93894-84-9.

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Basic Methanolysis of $(CF_3PCF_2)_2$: New Bis(phosphino)difluoromethanes and (Difluoromethyl)phosphines. NMR Resolution of Double-Phosphine Diastereomers

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The methoxide-catalyzed methanolysis of $(CF_3PCF_2)_2$ converts first the highly strained cis isomer (and then the trans), opening the ring to form $CH_3O(CF_3)PCF_2P(CF_3)CHF_2$ (abbreviation: "MeOPCP"). The secondary attack occurs at the CH_3OPCF_3 group to form HCF_3 and $(MeO)_2PCP$. Further P–C bond cleavages occur at various points, forming $(CH_3O)_3P$, $CH_3OP(CHF_2)_2$, $(CH_3O)_2PCHF_2$, and $CF_3P(CHF_2)_2$, disproportionation of which leads to $P(CHF_2)_3$. The highly vulnerable $CH_3OP(CF_3)CHF_2$ is not observed. HCl replaces CH_3O by Cl on P, with P_4O_{10} promoting the process by removing CH_3OH. Then either MeOPCP or ClPCP is converted, by base-catalyzed action of $Zn(CH_3)_2$, to MePCP, which forms a nonpolar BH_3 complex. Similarly, $CH_3OP(CHF_2)_2$ is chlorinated to $ClP(CHF_2)_2$, convertible by $(CH_3)_2NH$ to $(CH_3)_2NP(CHF_2)_2$. The ^1H NMR spectra of the CHF_2 groups in MeOPCP, ClPCP, MePCP, and MePCP·BH_3 show the expected P-chiral diastereomers as interlaced but resolvable triplets of doublets. The ^{19}F spectra of their CF_2 groups are separable and roughly interpretable as AB systems, except that F_A and F_B for P–CF_2–P are superposed in MePCP—but resolved in its BH_3 complex. These AB spectra, as well as those for most of the new $RP(CHF_2)_2$ compounds, are more complex at the fine-structure level, and not yet fully interpreted.

The base-catalyzed hydrolysis of P–CF_3 compounds, yielding P–OH compounds and HCF_3,[1] implies that a methoxide-catalyzed methanolysis of the P–CF_3 bond would give P–OCH_3 compounds and HCF_3. Similarly, any P–CF_2–P compound might be cleaved to form P–OCH_3 and HCF_2–P compounds. Thus an extensive methanolysis of either the cis or the trans isomer of $(CF_3PCF_2)_2$[2] could be expected to involve both reaction types, including ring cleavage to form open-chain P–CF_2–P compounds, convertible to interesting monophosphines. At each stage, one P–C bond could be more vulnerable than the others, according to rules worthy of discovery.

Indeed, a series of such methanolyses, using deficient portions of methanol, with removal of the volatile products at each stage and identification of these by NMR spectra, showed strong preference for four successive reactions:

$$(CF_3PCF_2)_2 + CH_3OH \rightarrow CH_3O(CF_3)PCF_2P(CF_3)CHF_2 \quad (1)$$

$$+ CH_3OH \rightarrow (CH_3O)_2PCF_2P(CF_3)CHF_2 + HCF_3 \quad (2)$$

$$+ CH_3OH \rightarrow (CH_3O)_3P + CF_3P(CHF_2)_2 \quad (3)$$

$$CF_3P(CHF_2)_2 + CH_3OH \rightarrow CH_3OP(CHF_2)_2 + HCF_3 \quad (4)$$

all occurring in the presence of the catalyst $NaOCH_3$.

The rates of these reactions are not very different, for the methanol-deficient experiments showed some formation of the products of reactions 3 and 4 before reaction 1 was complete. The main rules of selective reactivity here seem to be as follows:

1. Cleavage of the strained ring occurs exclusively before P–CF_3 cleavage. Indeed, using a mixture of the isomers, one observes complete elimination of the more strained cis form before much of the trans form has been consumed.

2. Attack at the methoxylated P atom is strongly favored.

3. Usually, P–CF_3 cleavage would be expected to occur before any P–CF_2X cleavage (cf. reaction 4; indeed, CH_2F_2 never was observed), but rule 1 governs reaction 1 and rule 2 governs reactions 2 and 3.

Although these rules seem very strong, some minor products indicate exceptions. All of the following possible processes would be expected to occur at least infinitesimally.

$$CH_3O(CF_3)PCF_2P(CF_3)CHF_2 + CH_3OH \rightarrow (CH_3O)_2PCF_3 + CF_3P(CHF_2)_2 \quad (5)$$

$$\text{or} \rightarrow CH_3O(CF_3)PCF_2P(CHF_2)OCH_3 + HCF_3 \quad (6)$$

$$\text{or} \rightarrow 2CH_3OP(CF_3)CHF_2 \quad (7)$$

$$(CH_3O)_2PCF_2P(CF_3)CHF_2 + CH_3OH \rightarrow (CH_3O)_2PCF_2P(CHF_2)OCH_3 + HCF_3 \quad (8)$$

$$\text{or} \rightarrow (CH_3O)_2PCHF_2 + CH_3OP(CF_3)CHF_2 \quad (9)$$

$$(CH_3O)_2PCF_2P(CHF_2)OCH_3 + CH_3OH \rightarrow (CH_3O)_3P + CH_3OP(CHF_2)_2 \quad (10)$$

$$\text{or} \rightarrow 2(CH_3O)_2PCHF_2 \quad (11)$$

$$CH_3OP(CF_3)CHF_2 + CH_3OH \rightarrow (CH_3O)_2PCHF_2 + HCF_3 \quad (12)$$

$$3R_2PCHF_2 \rightarrow 2R_3P + (CHF_2)_3P \quad (R = CH_3O \text{ or } CF_3) \quad (13)$$

Indeed, it may be suggested that the phosphines from reactions 9, 11, and 12 are formed by no other processes.

Reaction 13, an unexpected catalyzed disproportionation, was indicated by the frequent appearance of the ^{19}F and ^{31}P NMR spectra of $P(CHF_2)_3$ in crude $CF_3P(CHF_2)_2$.

Parallel to reaction 3 is a process yielding a nonvolatile oil, often representing as much as half of the phosphorus material. This

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could be due to Arbuzov-type reactions, from the products of which the desired volatile phosphines could not be recovered by further action of methanol and methoxide.

The methanolysis products are possible sources of many new phosphines and bis(phosphino)difluoromethanes, including interesting new ligands for displacement of CO from transition-metal carbonyls. The somewhat neglected CHF_2–P chemistry can be reached through the action of CHF_2I on P_4 (as shown in a subsequent paper) but it might be far more difficult to make PCF_2P compounds by such direct methods. For the fuller development of the PCF_2P chemistry, it is possible to convert $POCH_3$ to PCl compounds (e.g., by action of HCl in the presence of P_4O_{10}); then these can lead to far wider variety. An example is the conversion of $CH_3O(CF_3)PCF_2P(CF_3)CHF_2$ through the Cl–PCP derivative to $CH_3(CF_3)PCF_2P(CF_3)CHF_2$, as mentioned in an earlier paper.[2] The basic methanolysis of this methyl derivative also might be worthy of study: attack at the far P atom is expected. The products would be HCF_3 and $CH_3(CF_3)PCF_2P(CHF_2)OCH_3$ (with OCH_3 replaceable by CH_3) followed by interesting monophosphines.

Experimental Methods

Most of the high-vacuum methods here employed have been described in recent papers.[2] A special technique was devised for making and renewing catalytic traces of $NaOCH_3$. Molten sodium was drawn into glass capillary tubes (i.d. 0.5 mm); thus a measured length of enclosed sodium rod could be cut off and dropped into dry N_2, in a reaction tube connectable through an O-ring valve to the vacuum line. Then the sodium could be sublimed out of the capillary tube under high vacuum and treated with dry methanol. The resulting hydrogen, collected by the automatic Sprengel pump, was a measure of the resulting $NaOCH_3$. For anaerobic renewal of this catalyst, a short tube containing sodium could be introduced into the space above the closed O-ring valve, which then was connected through a ground-glass joint and a stopcock to the vacuum line. Thus the O-ring valve could be opened in vacuo, and the fresh sodium could be dropped into the reaction zone. Now the methanol would slowly act upon the encapsulated sodium, continuously forming minute amounts of new $NaOCH_3$.

For the $HCl–P_4O_{10}$ method of chlorinating methoxyphosphines, commercial $(P_2O_5)_x$ was sublimed under dry O_2, through an L-tube down into the reaction tube. The resulting very fluffy, high-surface P_4O_{10} was very efficient for removing the trace of methanol which the $HCl–CH_3OP{=}$ equilibrium would afford. This process avoids direct chlorination to P(V) compounds (except that the Arbuzov reaction may not be completely avoidable), but it does consume more than the calculated amount of HCl—most probably because the $POCH_3$ material formed from the P_4O_{10} is itself converted to nonvolatile P–Cl material. The yields of volatile chlorophosphines are far from quantitative, but usually well above 50%, and the products are easily purified.

NMR spectra were used to identify the products, to monitor their purification, and to analyze mixtures. The well-separated ^{19}F spectra proved to be the most directly useful, but the ^1H and ^{31}P spectra usually were employed for final confirmation of molecular structures. Much early work was done with the Varian XL100-FT instrument (later replaced by the Bruker WP270) and there was some use of the Varian XL200-FT instrument (operated by Dr. V. V. Krishnamurthy in our Hydrocarbon Institute) as well as the Bruker WM500 instrument at the Regional NMR Facility (at the California Institute of Technology)—uniquely effective for separation of the ^{19}F spectra of the PCP diastereomers. As before,[2] a positive δ (ppm) is upfield of Cl_3CF or H_3PO_4, but downfield from $(CH_3)_4Si$; and ${}_nJ_{WXYZ}$ means n-peak coupling of the observed nucleus W to $n-1$ half-spin Z nuclei.

Methanolysis Experiments and Products

Conditions and Procedures. Optimum experimental conditions for the methoxide-catalyzed methanolysis of $(CF_3PCF_2)_2$ have not been found: the possible combinations of variables would be too numerous. The first main plan was to run processes 1–4 successively, by repeated use of deficient amounts of methanol and frequent removal of the volatile products. However, $CH_3O(CF_3)PCF_2P(CF_3)CHF_2$ (hereinafter, "MeOPCP") never was the sole product; there was also some $(CH_3O)_2PCF_2P(CF_3)CHF_2$—called "$(MeO)_2PCP$"—as well as smaller yields of $CF_3P(CHF_2)_2$ and sometimes $CH_3OP(CHF_2)_2$ or $(CH_3O)_2PCHF_2$. The results were similar when MeOPCP was isolated and methanolyzed in the same way. However, methanolysis experiments beginning with $(MeO)_2PCP$ gave poor yields of monophosphines because at least 50% of it went to form nonvolatiles. It seemed better to operate in such a manner that $(MeO)_2PCP$ would be transient, always at low concentrations.

The second main plan was to aim for the monophosphines by starting with at least the amount of methanol required by eq 1–3. This way, there still was some recovery of the products of reactions 1 and 2 and little improvement in the yield of $CF_3P(CHF_2)_2$, but considerably more $CH_3OP(CHF_2)_2$ and $(CH_3O)_2PCHF_2$ were observed. In no experiment did the yield of monophosphines exceed 50%. For $CF_3P(CHF_2)_2$ the upper limit was about 20%; for $CH_3OP(CHF_2)_2$, about 35%; and for $(CH_3O)_2PCHF_2$, possibly 10%. The unexpected $P(CHF_2)_3$ was seen first as a minor complication in the ^{19}F NMR spectrum of impure $CF_3P(CHF_2)_2$. Its identity was confirmed by an authentic sample; also, the ^{31}P spectrum proved the molecular structure beyond doubt.

The ^{19}F spectra of the methanolysis products never showed any trace of the possible product $CH_3OP(CF_3)CHF_2$, the ^{19}F spectrum of which was recorded for an authentic sample. By reactivity rules 2 and 3, reaction 12 would have eliminated it.

Typical experiments are described in more detail as follows.

First Stage, with Mixed Isomers. An experiment employing 1.769 mmol of a 1:4 mixture of cis and trans $(CF_3PCF_2)_2$ with 0.526 mmol of methanol and 0.16 mmol of $NaOCH_3$, during 10 min at 25 °C, produced 0.245 mmol of MeOPCP and 0.05 mmol of HCF_3 (per reaction 2), directly confirming reaction 1. The process was continued with more methanol (0.344 mmol) and $NaOCH_3$ (final total 0.29 mmol), until the methanol was virtually all consumed. The total yield of MeOPCP was 0.720 mmol (70% of the consumed dimer). The second-stage product $(MeO)_2PCP$ amounted to 0.093 mmol (9%); HCF_3, 0.161 mmol; $CF_3P(CHF_2)_2$, 0.03 mmol (3%). Possible $CH_3OP(CHF_2)_2$ was not observed. The loss of volatile material amounted to 0.2 mmol of dimer.

The recovered dimer (0.745 mmol) proved to be pure trans isomer (mp −37 °C);[2] the cis isomer had been eliminated.

A confirmatory experiment, using a 2:1 ratio of pure trans isomer to methanol (three steps) gave a 75% yield of pure MeOPCP, 8% $(MeO)_2PCP$, and 7% HCF_3, all relative to the consumed dimer. The monophosphine fraction was not sorted out.

The main product MeOPCP was clearly identified by the NMR spectra of its component groups, with δ and J values consistent with the known spectra of other phosphines. Its volatility (0.8 mm at 0 °C and 5.0 mm at 27 °C) would suggest a normal boiling point near 151 °C if the Trouton constant is 21.0 eu. Having two asymmetric P atoms, it exists as two diastereomers, showing four AB-type ^{19}F NMR spectrta for the CF_2 groups—all separable by the WM500 instrument.

The Secondary Methanolysis. A typical experiment proving reactions 2 and 3 began with 0.197 mmol of MeOPCP, 0.097 mmol of methanol, and 0.019 mmol of $NaOCH_3$. During 2 min at 25 °C, there was vigorous effervescence due to HCF_3 (0.028 mmol); no CH_2F_2 could be found. The most and least volatile fractions were removed and the process was continued with addition of 0.045 mmol of methanol and 0.017 mmol of $NaOCH_3$, until failure to yield more HCF_3 indicated minimization of the methanol; used, 0.122 mmol. The yield of $(MeO)_2PCP$ was 0.083 mmol (68% of the consumed MePCP), and that of HCF_3, 0.103 mmol. The monophosphine fraction included a trace of methanol, making it difficult to estimate the yields of these products; however, a combination of ^{19}F NMR spectra and stoichiometry would suggest that there was no more than 0.02 mmol of $CF_3P(CHF_2)_2$, with far less $CH_3OP(CHF_2)_2$, and still less $(CH_3O)_2PCHF_2$.

The main liquid product, $(CH_3O)_2PCF_2P(CF_3)CHF_2$, showed only 1 mm volatility at 25 °C and so was easily separated from the unused MeOPCP. With only one asymmetric P atom, its NMR spectra were cleaner and simpler than those of the other PCP compounds. The proton, fluorine, and phosphorus spectra all were interpretable, leaving no doubt of the molecular structure.

Synthesis of $CF_3P(CHF_2)_2$. The best experiment intended for a maximum yield of $CF_3P(CHF_2)_2$ began with 0.945 mmol of $(CF_3PCF_2)_2$, of which 0.880 mmol was consumed. The process went at 25 °C in five steps, after each of which the HCF_3 and $CF_3P(CHF_2)_2$ (barely volatile at −78 °C) were removed. Only

at the end were the less volatile products removed: 0.027 mmol of MeOPCP, 0.292 mmol of $(MeO)_2PCP$, and uncertain yields of $CH_3OP(CHF_2)_2$, $(CH_3O)_2PCHF_2$, and $(CH_3O)_3P$, all of which (and especially the last) could have suffered diminution by conversion to less volatile material by the Arbuzov reaction.

The first two steps employed 0.045 mmol of $NaOCH_3$ with 0.910- and 0.424-mmol portions of methanol. The third step used 0.018 mmol of fresh $NaOCH_3$ and a final addition of 1.169 mmol of methanol. More $NaOCH_3$ (0.036 mmol) was added for the final step. The successive yields of HCF_3 were 0.132, 0.042, 0.509, 0.185, and 0.292 mmol. The corresponding fractions rich in $CF_3P(CHF_2)_2$ were 0.168, 0.022, 0.067, 0.013, and 0.018 mmol, to a total of 0.288 mmol. However, treatment with P_4O_{10} (to remove methanol) reduced this to 0.180 mmol, representing 20% of the consumed $(CF_3PCF_2)_2$. But then if we include the PCP products, the total recovery of products of interest exceeds 52%. By further use of the PCP compounds, the yield of $CF_3P(CHF_2)_2$ would be improved. Nevertheless, the present process may well be superseded by catalytic scrambling of $(CF_3)_3P$ and $(CHF_2)_3P$, both of which are more easily available than $(CF_3PCF_2)_2$.

Synthesis of $CH_3OP(CHF_2)_2$. An experiment aimed toward a maximal yield of $CH_3OP(CHF_2)_2$ began with 2.173 mmol of CH_3OH (total, 2.712; consumed, 2.431), 0.196 mmol of $NaOCH_3$ (total, 0.25), and 0.683 mmol of $(CF_3PCF_2)_2$ (consumed, 0.640). The reaction occurred in three effective stages, each with removal of the most volatile products. The yield of nearly pure $CH_3OP(CHF_2)_2$ (mol wt: found, 168; calcd, 164) was 0.224 mmol, representing 35% of the consumed dimer, on the basis of reactions 1–4. The PCP fraction was only 9.2 mg. Other volatiles could be estimated only roughly: 0.4 mmol of $(CH_3O)_3P$ and 0.08 mmol of $(CH_3O)_2PCF_3$. Not observable was $CF_3P(CHF_2)_2$; in view of the excess methanol, it could have been eliminated by reaction 4.

For better characterization, $CH_3OP(CHF_2)_2$ was made from $(CHF_2)_2PCl$, available through the P_4–CHF_2I process.

Other PCP Compounds

MeOPCP with HCl and P_4O_{10} efficiently formed ClPCP. Then either MeOPCP or ClPCP with $Zn(CH_3)_2$ and $(CH_3)_3N$ (catalyst) gave MePCP. Such methods would yield many other new PCP compounds.

Synthesis of ClPCP. The following equation with mmol quantities describes two experiments for chlorinating MeOPCP at 25 °C:

$$CHF_2(CF_3)PCF_2P(CF_3)OCH_3 + HCl \rightarrow CHF_2(CF_3)PCF_2P(CF_3)Cl$$

0.344	1.209	
−0.040	−0.734	0.242 (80%)
0.304	0.475	
0.461	0.856	
−0.159	−0.522	0.245 (82%)
0.302	0.334	

+ CH_3OH taken out by P_4O_{10}

The first of these experiments ran for 36 h; the second, for only 2 h. In both, the consumption of HCl was excessive, but more so for the longer run, as expected if the reason is its action on the nonvolatile MeOP product of absorption of methanol by P_4O_{10}.

The volatility of the product ClPCP (2.5 mmol at 0 °C and 13.0 mm at 26.5 °C) can be described by the equation $\log P = 6.2974 + 1.75 \log T - 0.005T - 2403/T$ (bp 130 °C; Trouton constant 21.45 eu). Its identity was proved beyond doubt by its NMR spectra.

Synthesis of MePCP. The diastereomeric compound $CH_3(CF_3)PCF_2P(CF_3)CHF_2$ was made in pure condition (with yields high but not well measured) by the action of equimolar $Zn(CH_3)_2$ upon either ClPCP or MeOPCP (during warming from −196 to +25 °C). Neither process went forward without catalysis, for which $(CH_3)_3N$ proved to be quite effective. When ClPCP was used, there was a slight excess of $Zn(CH_3)_2$ and slightly more than equimolar amine, because the nonvolatile solid product seems to be the amine complex of CH_3ZnCl. With MeOPCP, far less amine was used, and most of it was recoverable. In both cases, it was necessary to draw off all volatiles for further reaction (e.g., 16 h at 25–40 °C) to assure completion of the process. Then the final purification in a very small reflux column was fairly easy.

The pure MePCP showed exactly the same ^{19}F NMR spectrum (but without the obvious impurities) as was recorded for the major product of the uncatalyzed $(CH_3)_2Zn$–$(CF_3)_2PH$ reaction,[2] leaving no doubt of the identity of that product. New volatility measurements (1.3 mm at 0 °C, 3.46 mm at 14.24 °C, 14.08 mm at 38.0 °C, and 20.00 mm at 44.7 °C) determined the equation $\log P = 6.4180 + 1.75 \log T - 0.005T - 2513/T$ (bp 143 °C; Trouton constant 21.6 eu), differing little from the earlier 85% sample.[2]

The Borane(3) Complex of MePCP. A 0.174-mmol sample of MePCP (from the above authentic synthesis) was exposed to 0.125 mmol of B_2H_6, in a sealed Wilmad WGS 5BL NMR-insert tube. Two weeks later, the ^{19}F spectrum was obtained by means of the WM500 instrument, showing MePCP·BH_3 in 7:1 ratio to free MePCP. Thus the excess B_2H_6 would be 0.049 mmol. When the sample was returned to the vacuum line, the complex proved to be nearly as volatile as MePCP itself; it thus is in the nonpolar class, closely analogous to BH_3·CO, wherein π bonding of B–H electrons to C–O π^* orbitals neutralize the polarity.[4] Its instability prevented fuller characterization.

The NMR spectra of this complex are compared with those of MePCP itself in the separate section on NMR results. It is interesting that direct attachment of BH_3 to P pushes δ_P far downfield; but for the near CF_3 group, δ_F is moved upfield. Also of interest is the ^{19}F spectrum of the CF_2 connecting group. In MePCP the expected A and B branches are superposed and not recognizable, whereas in the BH_3 complex it is easy to sort out the two AB spectra of the diastereomers.

Monophosphine Conversions

The new monophosphine $CH_3OP(CHF_2)_2$ can lead to many other new $RP(CHF_2)_2$ compounds, of which two examples are here described.

An Aminophosphine. A crude sample of $CH_3OP(CHF_2)_2$ (not easily separable from the unused dimer after methanolysis) was converted by the HCl–P_4O_{10} method to $ClP(CHF_2)_2$, which was isolated and allowed to react with a twofold proportion of $(CH_3)_2NH$ during a warm-up from −196 to +25 °C. The resulting $(CH_3)_2NP(CHF_2)_2$ could be purified by simple high-vacuum distillation methods. Its molecular weight (for the nearly saturated vapor at 28 °C) was determined as 179 (calcd 177). Its volatility (2.9 mm at 0 °C and 18.6 mm at 29.6 °C) could be represented by the equation $\log P = 7.3976 + 1.75 \log T - 0.0065T - 2574/T$ (bp 124 °C; Trouton constant 21.2 eu).

The Chlorophosphine. The best sample of $(CHF_2)_2PCl$ came from the action of 2 equiv of HCl on pure $(CH_3)_2NP(CHF_2)_2$, during the usual slow warm-up from −196 °C. Its vapor density at 25 °C and 43 mm pressure gave the molecular weight as 170 (calcd 168.5). Its volatility (9.3 mm at −22.8 °C, 38.1 mm at 0 °C, 108.5 mm at 20.5 °C, and 143.0 mm at 26.2 °C) is described by the equation $\log P = 6.3024 + 1.75 \log T - 0.0057T - 2029/T$ (bp 70.8; Trouton constant, 21.4 eu).

The significant infrared frequencies of $(CHF_2)_2PCl$ (cm^{-1}; Beckman IR20A instrument) are here listed (with relative intensities in parentheses) with suggested assignments: C–H stretching 2965 sh (0.15), 2937 (0.38); C–H bending (?) 1328 sh (1.1); CF asymmetric stretching 1309 (3.5), 1286 (4.7); C–F symmetric stretching 1090 (31), 1066 sh (19); CF_2 deformation 777 (0.36), 770 (0.40), 736 (0.38), 685 (0.60); P–Cl stretching 511 (2.4). In-phase P–C stretching might be represented by 405 (0.14) but more probably all kinds of P–C stretching are covered by the stronger P–Cl stretching, possibly with coupling. Of primary interest here is the nearly 200 cm^{-1} difference between the C–F stretching frequencies, with very different intensities. For trifluoromethylphosphines, these differences are far smaller.

(4) Confirming calculations were done by: Ermler, W. C.; Glasser, F. D.; Kern, C. W. *J. Am. Chem. Soc.* **1976**, *98*, 3799.

Table I. ^1H and ^{31}P NMR Data for PCP Compounds

	δ_H	$^2J_{HCOP}$ or $^2J_{HCP}$	$^3J_{HCF}$	δ_P[a]	half-height width, s^{-1}
CH_3OPCP	3.50	13.0	...	−109	240
	6.456[b]	8.40	50.5	5	350
	6.410	8.4	50.5		
$(CH_3O)_2PCP$	3.07	11.8[c]	...	−157	26[d]
	6.47	13	50.1[e]	4	*f*
ClPCP	6.511[g]	6.74	50.7	−63	240
	6.478[g]	6.48	50.6	8	350
CH_3PCP	1.31	5.1	...	−3.4	(Figure 1)
	6.484[b]	6.7	50.3	6.7	(Figure 1)
	6.450	7.0	50.1		
$CH_3PCP{\cdot}BH_3$[h]	1.64	9.9	...	−58.4	306
	6.599[b]	14.1	49	1.8	293
	6.587	14.5	49		

[a] The positive values of δ_P represent the CF_3PCHF_2 group. [b] The weaker diastereomer (for CH_3PCP the ratio is 3:4). [c] $^2J_{HCOPCP} = 3.52$. [d] $^3J_{PCF} = 138$; the broad peaks are split at the tops, with apparent separations near 5.6 s^{-1} for pseudoquartets. [e] "J" = 0.9 for the mixed pattern of $^2J_{HCPCP}$ and $^4J_{HCPCF}$. [f] Good resolution permitted full analysis: $^4J_{PCF} = 68.4$; for P-CF_2, $^2J = 152$ or 85 (from F spectrum 151, 84); for P-CHF_2, $^2J_{PCF} = 46$ or 57 (F spectrum 45, 56) and $^2J_{PCH} = 12$. $^2J_{PCP}$ could not be observed. [g] Equally intense diasteromers. [h] For protons on boron, $\delta = 0.6$, with two peaks indicating a normal value for $^4J_{HB}$, 94 s^{-1}. However, the overall peak to peak distance is 312, with one peak obscured by CH_3. There may be some diastereomeric separation, difficult to confirm.

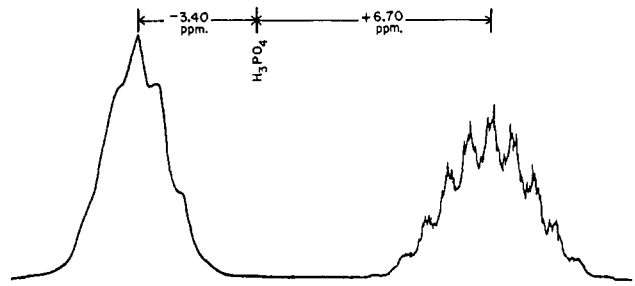

Figure 1. ^{31}P NMR spectrum of MePCP (WP270 instrument). The unsymmetrical downfield part (CH_3PCF_3 group) may be the result of skew superposition of the diastereomers. The upfield part (CHF_2PCF_3 group) might owe its moderate resolution, into eleven discernible clusters, to an approximate congruence of the δ separation of the diastereomers with the J_{PCF} values.

NMR Spectra

The tables compare NMR results for the phosphines as "neat" liquids in insert-tubes surrounded by acetone-d_6. Let it be repeated that δ is positive upfield of Cl_3CF or H_3PO_4 but downfield of $(CH_3)_4Si$ for ^1H. Frequencies ($\Delta\nu$ and J) are in the unit s^{-1} ("Hz"), and $_711$ (for example) means $J = 11$ with 7 peaks.

For each diastereomeric mixture, each CF_2 group gives a pattern governed by AB mathematics. Thus $D = [(\Delta\nu)^2 + {}^2J_{FCF}{}^2]^{1/2}$, measured by the frequency differences $B_i - A_o$ or $B_o - A_i$ for the inner and outer clusters. The intensity ratio $R = I_o/I_i$ is given by $(1 - J/D)/(1 + J/D)$, wherein $^2J_{FCF} = A_i - A_o = B_o - B_i$. Then δ_A and δ_B are measured as $\pm 0.5\Delta\delta$ (derived from $\Delta\nu$) from the main center. For the PCP compounds, only the WM500 instrument could be used, for maximum distance between the isomers, for adequate distance between A and B centers, and for an intensity ratio R large enough for the outmost clusters to be analyzable. It some cases, greater than AB complexity may be recognized, but the related fine couplings would be very difficult to sort out.

Proton and Phosphorus Spectra of PCP Compounds. Table I shows the simplest evidence of diastereomerism: ^1H spectra that are interlaced but not superposed. The comparison of δ values in each compound is accurate, but between compounds uncertainty is caused by diamagnetic effects. The ^{31}P spectra are mostly quite unresolved, except for the simple case of $(MeO)_2PCP$; and some information is found for the case of MePCP; cf. Figure 1.

Table II. Fluorine Spectra of MeOPCP

group		δ	$^2J_{FCP}$	$^2J_{FCPCP}$	$^nJ_{FCPCF}$
CF_3 near CHF_2		49.360	70.8	ca. 16	6-9
		49.408	71.5	ca. 16	6-9
CF_3 near MeO		63.559	83.1	17.4	7.7
		63.904	82.6	21.0	9.7
CHF_2[a]	A-1	116.657	149	?	?
	B-1	118.816	126	?	?
	A-2	117.361	134	15	10, 6
	B-2	119.261	115	?	?
PCF_2P[b]	A-1	103.8	160, 48	?	?
	B-1	106.1	90 av	?	?
	A-2	105.9	140, 45	?	?
	B-2	106.8	90 av	?	?

[a] For isomer 1, $^2J_{FCF} = 328$ and $R = 0.55$; for isomer 2, 348 and 0.46. Also, $^2J_{FCH}$ is 50.5 for A-1, 50.8 for B-1, 50.3 for A-2, and 50.2 for B-2. [b] For isomer 1, $^2J_{FCF} = 338$ and $R = 0.24$; for isomer 2, 331 and 0.11.

Table III. Fluorine Spectra of $(MeO)_2PCP$

group		δ	$^2J_{FCF}$	$^2J_{FCP}$	$^2J_{FCPCP}$	$^2J_{FCPCF}$
CF_3		49.0	...	68.5	(10)	(6.4)
PCF_2P	A	110.30	333.3	139, 45	(9)	(6.5)
	B	111.24	333.3	136, 56	(10)	(7.6)
CHF_2	A	117.60	335.2	151	(13)	(6.5)
	B	119.59	334.5	84	(10)	(7.6)

Table IV. Fluorine Spectra of ClPCP

group		δ	$^2J_{FCF}$	$^2J_{FCP}$	$^2J_{FCPCP}$	$^nJ_{FCPCF}$
CF_3 near Cl		50.8830	...	72	16	7-10
		51.0286	...	72	16	7-10
CF_3 near CHF_2		60.5238	...	81.2	16.7	9.5
		60.6762	...	81.3	17.5	9.4
PCF_2P	A	101.836	310	91, 50	...	?
	B	103.103	310	90 av	...	?
CHF_2	A-1	117.87	356	92?	?	?
	B-1	120.16	356	135	?	?
	A-2	117.815	355	130	?	?
	B-2	120.522	355	129	?	?

Fluorine Spectra of MeOPCP. Table II gives the ^{19}F results for $CH_3O(CF_3)PCF_2P(CF_3)CHF_2$. Here the CF_3 group adjacent to CH_3O is pushed upfield by π electrons from O, and the clusters can be sorted out to give the different J values for coupling to the A and B fluorine atoms in the connecting CF_2 group. The clusters for the downfield CF_3 group are more confused.

The CHF_2 group showed enough undisturbed clusters for direct determination of the main J values, but only the inner A branch of isomer 2 was resolved well enough for rough estimation of $^2J_{FCPCP}$, $^3J_{FCPCF}$ (10), and $^4J_{FCPCF}$ (6). The distance between outermost peaks for A_1 was 51, for B_1, 37, and for B_2, 35 s^{-1}; these were 11-peak patterns with inexact superposition.

The main AB interpretation of the connecting CF_2 group was more difficult because the B branches for the two isomers could not be sorted out by immediate observation. However, the A_o and A_i patterns for each isomer could be sorted out; then from the observed values of R and $^2J_{FCF}$ the D and $\Delta\nu$ values could be calculated—giving δ for Table II. With this information, it was possible to find in the B branches observable patterns consistent with the calculated values within 0.1 ppm.

The Dimethoxy Compound. Having only one chiral P atom, the compound $(CH_3O)_2PCF_2P(CF_3)CHF_2$ has only two AB spectra (Table III), easily assignable. However, the J_{FCPCP} and J_{FCPCF} values are uncertain on account of superposition and mixing. For the connecting CF_2 group, $R = 0.25$ on the WM500 or 0.06 on the XL100 instrument, and for CHF_2, 0.51 or 0.19, close to the calculated values. The $^2J_{FCP}$ values 136 and 139 are assigned to CF_2 coupling to $P(OCH_3)_2$, by reference to Table I, footnote *d*; and $^2J_{FCH} = 50.3$ s^{-1}.

The ClPCP Compound. Table IV shows the ^{19}F NMR data for $Cl(CF_3)PCF_2P(CF_3)CHF_2$. Here the CF_2 aspect is confused: instead of thirty-two clusters for two AB patterns (each with four

Table V. Fluorine Spectra of MePCP and MePCP·BH_3

group	δ	$^2J_{FCF}$	$^2J_{FCP}$	$^2J_{FCPCP}$	^nJ
CF_3PCH_3	56.6083[a]	...	72.5	18.5	8.4
	56.7177	...	72.4	18.6	8.3
CF_3PCHF_2	49.63[a]	...	72.0	17	8.5
	49.77	...	71.6	13?	7?
PCF_2P	101.9		60?	?	?
CHF_2[b] A-1	116.5059	353.7	143.1	*c*	6.4
B-1	119.0941	353.7	124.8	*c*	6?
A-2	116.3454[a]	353.9	136.0	*c*	6.4
B-2	119.2546[a]	353.9	123.6	*c*	6?
$CF_3PCH_3·BH_3$	62.010[a]	...	72.3	...	7–9
	62.359	...	72.7	15?	7?
CF_3PCHF_2	48.419[a]	...	74.4	?	?
	48.731	...	75.5	?	?
PCF_2P A-1	102.820	335	100	?	5–11?
B-1	104.540	335	90	?	7–10?
A-2	103.112[a]	333	75	?	5–8?
B-2	105.246[a]	333	100	...	...
CHF_2 A-1	116.327	345	28?	*c*	?
B-1	118.466	345	103[d]	*c*	7.7
A-2	116.368[a]	345	(small)	*c*	?
B-2	118.457[a]	345	103[d]	*c*	7.7

[a] The weaker isomer; ratio for MePCP 0.72. [b] For the stronger isomer (1), $R = 0.53$ (calcd 0.56); for the weaker (2), $R = 0.61$ (calcd 0.60). As usual, $^2J_{FCH} = 50.5$. [c] Confused with ^nJ, which includes $^3J_{FCPCF}$ and $^4J_{FCPCF}$. [d] Since B-1 and B-2 are almost perfectly superposed, one sees for either B_i or B_o four almost equal septets, giving $^2J_{FCP}$ as 103 and $^2J_{FCH}$ as 50.1. For isomer 1, $R = 0.51$, and for isomer 2, $R = 0.46$. In PCF_2P, $R_1 = 0.45$ and $R_2 = 0.52$.

Table VI. Proton NMR Data for Monophosphines

	δ	$^3J_{HCF}$	$^2J_{HCOP}$	$^2J_{HCP}$
$CF_3P(CHF_2)_2$	6.4	50.6	...	13.1
$P(CHF_2)_3$	6.22	50.3	...	15.3
$CH_3OP(CHF_2)_2$	3.51	...	12.8	...
	6.11	51.2	...	14.5
$(CH_3O)_2PCHF_2$	4.0	...	11.0	...
	6.06	51.0	...	7.13
$CH_3OP(CF_3)CHF_2$	3.40	...	12.9	...
	5.78	51.0	...	6.5
$ClP(CHF_2)_2$	5.51	50.9	...	18.6
$(CH_3)_2NP(CHF_2)_2$	3.31	...	8.47[a]	...
	6.80	50.7	...	16.05

[a] For HCNP.

clusters for each of the four branches), there are only sixteen clusters, wherein the peaks for the two isomers are hopelessly interlaced and superposed. Thus it is possible to report only average data for the two spectra, with $R = 0.32$ for both (calcd 0.36). The CHF_2 group is more intelligible, for $^2J_{FCH}$ values between 50.5 and 50.9, and calculated $R = 0.576$, aided the consistent selection of clusters. However, no great accuracy can be claimed for any of the four-bond coupling constants.

Comparison of MePCP with Its Borane(3) Complex. The ^{19}F spectra of MePCP and its BH_3 complex (with BH_3 on the MeP part) are described by Table V. The most striking contrast here is in the PCF_2P part: in the BH_3 complex this gives analyzable AB spectra whereas for MePCP itself there is only a messy central triplet for which "J" = 60, assignable as an average value for $^2J_{FCP}$. It seems that R and $\Delta\delta$ for both isomers are so small that the two F atoms are to be regarded as virtually δ-equivalent. Such equivalence would be ascribed to a structural accident, since the rate of isomeric conversion (inversion of pyramidal PX_3) cannot be expected to be faster than the time scale of the WM500 instrument.

The Monophosphine NMR Spectra. The WP270 results for the pertinent monophosphines are summarized by Tables VI–VIII. For the ^{19}F spectra, all of the AB calculations gave R values in agreement with the observed relative intensities. However, for $CH_3OP(CHF_2)_2$, $ClP(CHF_2)_2$, and $(CH_3)_2NP(CHF_2)_2$, the obvious asymmetry of all clusters, exemplified by Figure 2, requires

Table VII. Phosphorus NMR Data for Monophosphines

	δ	$^nJ_{PCF}$	$^nJ_{PCH}$	$^nJ_{POCH}$
$CF_3P(CHF_2)_2$	18.5	^{3}117.41	^{3}13.2	...
		^{3}115.77		
		^{4}68.1		
$P(CHF_2)_3$	23.5	^{7}105	^{4}15.0	...
$CH_3OP(CHF_2)_2$	−97	^{3}117.0	^{3}14.45	^{4}12.85
		^{3}109.5		
$(CH_3O)_2PCHF_2$	−147	^{3}131	^{2}7.13	^{7}11.0
$CH_3OP(CF_3)CHF_2$	−96[a]	^{2}143.5	^{2}6.34	^{4}12.9
		^{2}135.8		
		^{4}75.6		
$ClP(CHF_2)_2$	−46	^{5}107.6 av	^{3}18.7	...
$(CH_3)_2NP(CHF_2)_2$	−98.7	^{5}118 (half-height width 45)		

[a] 1.169 ppm upfield of the impurity $CH_3OP(CHF_2)_2$.

Table VIII. Fluorine NMR Data for Monophosphines

group		δ	$^2J_{FCP}$	$^2J_{FCH}$	$^nJ_{FCPCF}$
$CF_3P(CHF_2)_2$	CF_3	52.5	68.7	...	^{5}6.42
	CHF_2	120.2	117.3	50.5	^{4}6.35
$P(CHF_2)_3$		120.4	104.6	50.9	...
$CH_3OP(CHF_2)_2$	A	130.228	110.4	50.0	*a*
($^2J_{FCF} = 347$)	B	130.983	116.6	51.1	*a*
$(CH_3O)_2PCHF_2$		137	131	51.0	...
$CH_3OP(CF_3)CHF_2$	CF_3	67.3	75.6	51.0	^{3}7.02
($^2J_{FCF} = 334$)	CHF_2 A	130.184	135.25	50.8	^{4}7.2
	B	131.363	143.2	51.2	^{4}6.8
$ClP(CHF_2)_2$	A	122.6014	101.5	50.1	*a*
($^2J_{FCF} = 334$)	B	126.1875	112.7	51.5	*a*
$(CH_3)_2NP(CHF_2)_2$	A	125.6543	121.1	51.5	*a*
($^2J_{FCF} = 340$)	B	128.4171	116.1	50.1	*a*

[a] Unsymmetrical clusters; see text.

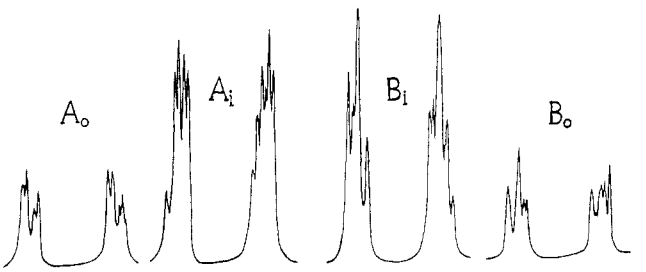

Figure 2. Eight of the sixteen clusters constituting the ^{19}F NMR spectrum of $(CH_3)_2NP(CHF_2)_2$ (WP270 instrument). Each pair of unlike clusters is closely duplicated at a frequency distance equal to $^2J_{FCP}$. The distance between members of each pair is $^2J_{FCH}$, always near 50. For consistent measurement of this J, the position of each cluster was determined as an average weighted by the intensities of the peaks. The analogous XL100 spectrum shows a similar system of sixteen unsymmetrical clusters, but with shapes very different from those here shown.

interpretation as AA'BB'PHH' systems. This means that one must consider four appreciably different values for each of $^2J_{FCP}$, $^2J_{FCH}$, $^2J_{FCPCF}$, and $^2J_{FCPCH}$—and possibly two for $^2J_{FCF}$. However, symmetry leads to identical values for some of these; for example, in $(CH_3)_2NP(CHF_2)_2$ there seems to be constancy for $^2J_{FCF}$ and for $^2J_{FCP}$ in either the A or the B branch. A first trial at computer simulation, using the PANIC program of the WP270 instrument with the observed $^2J_{FCF}$ and $^2J_{FCP}$ values along with reasonable sets of the values for $^2J_{FCH}$ (50–52), $^2J_{FCPCF}$ (6–7), and $^2J_{FCPCH}$ (4.2–4.5) gave a pattern similar in principle to Figure 2. However, for an exact match of each spectrum, much more time may be needed—beyond the immediate purpose.

The ^{19}F spectrum of $ClP(CHF_2)_2$ shows slightly unsymmetrical clusters, but with poor resolution. The full complexity here is found in the ^1H spectrum. Its $^2J_{HCP}$ is constant, so that each doublet has exactly similar members, but differs wildly from the other members of the main J_{HCF} triplet. The downfield doublet shows crooked quartets with apparent $J = 1.63$. Each member of the central doublet has a broad central peak, with a small, sharp upfield shoulder and outer spikes 7.04 s^{-1} apart. Each cluster of the upfield doublet is almost symmetrical, with central peaks

trifurcated ("J" = 0.75) and almost equal outer spikes 7.03 s^{-1} apart.

For $CF_3P(CHF_2)_2$, the ^{19}F spectrum lacks apparent complexity: there are only four slightly irregular clusters. Comparison of cluster widths in the XL100 and WP270 spectra shows that the $\Delta\delta$ for an AB spectrum cannot exceed 0.3 ppm; then R cannot exceed 0.0005. But the ^{31}P spectrum does show two values for J_{PCF}, proving that P couples to equivalent pairs of magnetically nonequivalent F atoms. Thus there is at least AB complexity, but with the A and B fluorine atoms almost perfectly superposed. The ^1H spectrum consists of four unsymmetrical triplets for which J_{HCPCF} is near 4.5; more than AB complexity is suggested, but the fine structure is not resolved well enough for analysis.

The adventitious product $P(CHF_2)_3$ was seen first in the ^{19}F spectrum (XL100 instrument), 0.1818 ppm upfield of $CF_3P(CHF_2)_2$, neatly interlaced without superposition of any peaks. The present data are for a pure sample made by the P_4–CHF_2I reaction, yet to be described. Omitted from Tables VI and VIII are $_5J_{HCPCF}$ = 4.3 and $_3J_{FCPCH}$ = 4.25, confirming that these are J values suitable for use in computer simulation of other $RP(CHF_2)_2$ spectra. This is far stronger coupling than ever before seen for HCPCF chains.

The ^{19}F spectrum of $CH_3OP(CF_3)CHF_2$ (recorded for an authentic sample) would have interlaced with or superposed upon $CH_3OP(CHF_2)_2$, but no sample from the dimer methanolysis ever showed any trace of such confusion.

Acknowledgment. I am grateful to the operators of the XL200 and WM500 instruments for some of the NMR spectra and to Dr. K. L. Servis for aid with difficult interpretations.

Registry No. $CH_3O(CF_3)PCF_2P(CF_3)CHF_2$ (isomer I), 94110-48-2; $CH_3O(CF_3)PCF_2P(CF_3)CHF_2$ (isomer II), 94110-49-3; HCF_3, 75-46-7; $(CH_3O)_3P$, 121-45-9; $CF_3P(CHF_2)_2$, 94110-50-6; $CH_3OP(CHF_2)_2$, 94110-51-7; $(CH_3O)_2PCF_2P(CF_3)CHF_2$, 94110-52-8; *cis*-$(CF_3PCF_2)_2$, 86350-48-3; *trans*-$(CF_3PCF_2)_2$, 86350-50-7; MeOH, 67-56-1; $(CH_3O)_2PCHF_2$, 4669-85-6; $P(CHF_2)_3$, 94110-53-9; $CHF_2(CF_3)PCH_2P(CF_3)Cl$, 94110-54-0; $CH_3(CF_3)PCF_2P(CF_3)CHF_2$ (isomer I), 86350-51-8; $CH_3(CF_3)PCF_2P(CF_3)CHF_2$ (isomer II), 86350-52-9; $ClP(CHF_2)_2$, 94110-56-2; $(CH_3)_2NP(CHF_2)_2$, 94110-57-3.

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Ethanol Oxidation by Chromium(III) Complexes of Chloranilic Acid. Spectroscopic, Electrochemical, Magnetic, and Chromatographic Studies of Chloranilate Semiquinone-Bridged Polynuclear Chromium Ions

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The oxidation of ethanol by chloranilic acid (H_2CA_{ox}; 2,5-dihydroxy-3,6-dichlorobenzoquinone), catalyzed by Cr(III), has been reexamined. Rate and spectrophotometric studies showed that a binuclear complex of the form $Cr_2(CA_{ox})^{4+}$ is the most reactive catalyst species; reduction of $Cr_2(CA_{ox})^{4+}$ is first order with respect to ethanol (95–99%), with a rate constant of 1.5×10^{-3} M^{-1} s^{-1} (60 °C). Spectrophotometric, chromatographic, magnetic susceptibility, electron paramagnetic resonance, and cyclic voltammetric measurements on the reduced chloranilate- (CA_r-) containing catalyst reduction product are also reported. Both 2:1 (I) and 5:2 Cr–CA_r complexes, with intense absorption maxima at 300, 355, 428, 458, 494, 600, and 654 nm, are formed in ethanol/water solutions. Binuclear complex I in 99% ethanol exhibits an effective magnetic moment per Cr atom of 3.81 μ_B (298.2 K), near the spin-only value for three unpaired electrons, an EPR resonance at g = 1.97 (100 K), and a quasi-reversible cyclic voltammogram (0.1 M $(n\text{-}C_4H_9)_4NClO_4$, 25.0 °C) indicative of a two-electron oxidation with $E_{1/2}$ = +0.46 V vs. SCE. Cation-exchange separations on SP-Sephadex C-25 resin confirmed the stoichiometry of I and demonstrated that its immediate oxidation product rapidly decays to give $Cr(H_2O)_6^{3+}$ and a 1:1 complex ($Cr(CA_{ox})^+$) in aqueous acidic solution. The 400–500-nm spectra of I and the chloranilate semiquinone trianion radical ($CASQ^{3-}$) are remarkably similar, suggesting that the predominant resonance form of I is Cr(II)–bridging $CASQ^{3-}$–Cr(III) rather than Cr(III)–bridging chloranilate hydroquinone–Cr(III). Qualitative molecular orbital arguments are presented to reconcile the magnetic results with this hypothesis and account for the electronic spectra of $CASQ^{3-}$ and I.

Introduction

Benzoquinones with electron-withdrawing substituents, such as chloranil (tetrachloro-1,4-benzoquinone), are versatile two-electron oxidants in organic synthesis.[1] Quinones are prime candidates as electron acceptors in alcohol-oxidizing fuel cell catalysts, as the electrochemical reversibility of most quinone/hydroquinone couples is excellent.[2] Furthermore, the capability of certain activated quinones to convert alcohols into the corresponding carbonyl compounds is already documented.[3,4] The catalytic potential of benzoquinones is considerably enriched through the coordination of these ligands to transition-metal ions.[5] For example, iron–quinone complexes serve as efficient electron carriers in mitochondria and in bacterial photosynthetic systems.[6,7]

An intriguing report by Linck and Taube suggests that chromium(III) complexes of 2,5-dihydroxy-1,4-benzoquinone (H_2DHBQ) and chloranilic acid (H_2CA, 2,5-dihydroxy-3,6-dichloro-1,4-benzoquinone) may serve as ethanol oxidation catalysts under mild conditions (25 °C), yielding acetaldehyde as the sole organic product.[8] Acetaldehyde is formed more rapidly through the action of strong transition-metal oxidants (i.e. MnO_4^-, $Cr_2O_7^{2-}$) on ethanol in aqueous solution,[9] but the electrochemical irreversibility of these oxidants prevents their use as catalysts. Furthermore, most of the free energy released in the C_2H_5OH–O_2

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