even larger $\Delta E_p = 1.15$ V for $[Mn(edt)_2(HIm)]^-$[12] (v and scan limits unspecified) presumably arises in the same way. $[Mn(tdt)_2]^-$ is reported to be reduced at $E_{p,c} = -1.09$ V with $\Delta E_p = 0.61$ V in a DMF solution at a Pt electrode (v = 100 mV/s).[11] We have reproduced this result and also have shown that at a GC electrode ΔE_p is diminished to 0.11 V (Table I). This behavior closely resembles that in Figure 8 and is ascribed to significantly different k_s values at the two electrode surfaces. While the reduction/oxidation cycle of $[Mn(edt)_2(solv)_2]^-$ (reactions 14 and 16) must involve the structural and spin changes previously described,[1] it is now evident that the large ΔE_p values observed in Mn–edt and Mn–tdt systems do not demonstrably derive from them. Instead, any such kinetics effects arising in this way that would cause deviations from reversible charge transfer are overridden by slow heterogeneous electron transfer and adsorption. This is made particularly evident by reaction 18 in acetonitrile, which carries

$$[Co(edt)_2]^- \text{ (planar, } S = 1) + e^- \xrightleftharpoons{-1.16\text{ V}} [Co(edt)_2]^{2-} \text{ (tetrahedral, } S = {}^3/_2) \quad (18)$$

a structural and a spin change (involving σ^* orbitals). Under the same conditions where the Mn systems exhibit large ΔE_p values, this reaction is one of reversible charge transfer (Table I). As in at least one prior case,[59b] examination of redox reactions at more than one electrode surface has shown that interpretation of large ΔE_p values solely in terms of structural changes accompanying charge transfer is incorrect. The electrochemistry associated with numerous processes of this type has been characterized.[54,65]

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Registry No. **2** (M = Mn^{III}), 87526-32-7; **2** (M = Fe^{III}), 46847-88-5; $[Ti(edt)_3]^{2-}$, 94750-77-3; $[V_2(edt)_4]^{2-}$, 87145-61-7; $[Cr(edt)_2]^{2-}$, 94750-79-5; $[Mn(edt)_2]^{2-}$, 87526-34-9; $[Fe(edt)_2]^{2-}$, 102920-35-4; $[Co(edt)_2]^-$, 94750-83-1; $[Co(edt)_2]^{2-}$, 94750-82-0; $[Mn(tdt)_2]^{2-}$, 94595-52-5; $[Mn(tdt)_2]^-$, 94500-28-4; $[Fe(tdt)_2]^-$, 14874-42-1; $[Co(tdt)_2]^-$, 52152-14-4; $[Mn(edt)_2(Me_2SO)]^-$, 102920-36-5; $[Mn(edt)_2(Me_2CN)_2]^-$, 87802-61-7; $[Fe(edt)_2(Me_2CN)_2]^-$, 102920-37-6; Pt, 7440-06-4; carbon, 7440-44-0; graphite, 7782-42-5.

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Solution Chemistry of Rhodium Trifluoroacetate in the Presence of Phosphorus Donors

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$^{31}P\{^1H\}$ and ^{19}F NMR studies on $Rh_2(O_2CCF_3)_4(PY_3)_2$ where Y = OPh, Ph, or Cy (cyclohexyl) are described. The $^{31}P\{^1H\}$ NMR spectrum of the $P(OPh)_3$ adduct shows an AA′XX′ (A, A′ = ^{103}Rh; X, X′ = ^{31}P) system, as expected for an axial (class I) adduct. A single ^{19}F signal is observed. A similar spectrum is also seen for $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$. The $^{31}P\{^1H\}$ NMR spectra of the PPh_3 and PCy_3 adducts both show three signals due to the presence in solution of an axial (class I) and axial/equatorial (class III) phospine coordinated Rh dimer. This solution behavior is in contrast to their class I solid-state structure. $Rh_2(O_2CCF_3)_4$ reacts with excess PCy_3 to give monomeric Rh(I) and Rh(III) species. The $^{31}P\{^1H\}$ and ^{19}F NMR spectra of $Rh(O_2CCF_3)_2(P(OMe)_3)_3$ are reported and support the true formulation of the complex as $Rh(P(OMe)_3)_4{}^+Rh(O_2CCF_3)_4(P(OMe)_3)_2{}^-$. A mechanism is proposed for cleavage of the Rh^{II}_2 complex to Rh(I) and Rh(III) monomers involving ligand-induced polarization of the Rh–Rh bond.

Introduction

Complexes of general formula $Rh_2(O_2CR)_4L_2$ have been widely studied in the solid state,[1] and all have axially coordinated Lewis bases. This structural type has been called class I by Andersen.[2] With $Mo_2(O_2CCF_3)_4$, Lewis base coordination equatorial to the Mo–Mo bond has been reported in the solid state[2,3] and in solution[4] to give what are referred to as class II complexes.[2] In a previous study from this laboratory,[5] we found that both axial and equatorial ligand coordination occurred to one dimeric $Rh_2(O_2CCF_3)_4$ unit in the presence of excess pyridine and *tert*-butyl isocyanide, which we call class III behavior. Furthermore, it was found that with phosphorus donors unusual solution behavior was observed even without excess ligand. In the presence of excess ligand, Rh–Rh bond cleavage occurred much more readily with phosphorus than with other donors. We have extended and clarified these earlier studies and find definitive evidence for the unusual behavior of $Rh_2(O_2CCF_3)_4$ in the presence of phosphorus donor bases.

Results and Discussion

The previously reported[5] ^{19}F NMR spectrum of $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$ (before decomposition occurred) showed a single peak corresponding to the four equivalent $CF_3CO_2^-$ ligands, suggestng a class I (axial) structure in solution.

The $^{31}P\{^1H\}$ NMR spectrum of $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$ obtained earlier in $CDCl_3$ at room temperature on a 100-MHz instrument provided inconclusive structural information since extensive ligand oxidation occurred to form $OP(OPh)_3$.[5] In the present study a 300-MHz ^{1}H (121.5 MHz for ^{31}P) instrument was used, which gave better resolution, required less data aquisition time, and required less sample. Furthermore, the $CDCl_3$ solution of $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$ was frozen at −70 °C immediately after prepartion to inhibit the phosphite oxidation process. The $^{31}P\{^1H\}$ NMR spectrum of $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$ obtained in this manner showed no signal attributable to phosphate. The $^{31}P\{^1H\}$ NMR signal obtained here showed a quartet, but with the center peaks very close at −50 °C. $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$ is an AA′XX′ spin system (A, A′ = ^{103}Rh; X, X′ = ^{31}P). The outer lines are separated by $|J_{AX} + J_{AX'}| = |{}^1J_{Rh-P} + {}^2J_{Rh-P}| =$ 134.5 Hz. All ^{31}P NMR data are summarized in Table I. The separation of the inner lines (11.5 Hz at −150 °C) is either $[((J_{AA'}$

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Table I. Summary of Low-Temperature ^{31}P NMR Data in $CDCl_3$ Solution for Rhodium Carboxylate Complexes with Phosphorus Donors

complex	class of NMR spectrum	chem shift, ppm rel to 85% H_3PO_4	coupling const, Hz
$Rh_2(O_2CCH_2CH_2CH_3)(PPh_3)_2$	AA′XX′ (A, A = ^{103}Rh; X, X′ = ^{31}P)	$\delta_{X,X'} = -20.0$	$J_{inner} = 10.8$, $J_{outer} = 88.3$[a]
$Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$	AA′XX′ (assignt as above)	$\delta_{X,X'} = +69.5$	$J_{inner} = 11.5$, $J_{outer} = 134.5$[a]
$Rh_2(O_2CCF_3)_4(PPh_3)_2$	AA′XX′ (assignt as above)	$\delta_{X,X'} = -15.1$	$J_{inner} = 13.0$, $J_{outer} = 81.2$[a]
	ABXY, 3:1 (A = ^{103}Rh(eq); B = ^{103}Rh(ax); X = ^{31}P(eq); Y = ^{31}P(ax))	δ_X = 5.B 34.2 (doublet of doublets), $\delta_Y = -23.2$ (doublet of doublets)	$J_{AB} = (8)$, $J_{AX} = 164$, $J_{AY} = 26.8$, $J_{BX} = 0$, $J_{BY} = 92$, $J_{XY} = 11.7$[b]
$Rh_2(O_2CCF_3)_4(PCy_3)_2$	AA′XX′ (assignt as above)	$\delta_{X,X'} = -7.80$	$J_{inner} = 14.6$, $J_{outer} = 84.1$[a]
	ABXY, 2:1 (assignt as above)	$\delta_X = 32.2$ (doublet of doublets), $\delta_Y = -13.7$ (doublet of doublets)	$J_{AB} = (8)$, $J_{AX} = 164$, $J_{AY} = 25$, $J_{BX} = 0$, $J_{BY} = 90$, $J_{XY} = 12.0$[b]
$Rh_2(O_2CCF_3)_2[P(OMe)_3]_3$ (empirical formula:	AX	$\delta_X = 89.5$	$J_{AX} = 132.5$
$[Rh(O_2CCF_3)_4(P(OMe)_3)_2]^-$ $[Rh(P(OMe)_3)_4]^+$)	A′X′ 1:2 (A = ^{103}Rh(III); A′ = ^{103}Rh(I); X = ^{31}P(–Rh(III)); X′ = ^{31}P(–Rh(I)))	$\delta_{X'} = 135.0$	$J_{A'X'} = 181.5$

[a] Since only four of the ten nondependent peaks in an AA′XX′ spectrum was observed, unique analyses of these spectra are not possible. Nevertheless, simulations suggest that for $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$, $Rh_2(O_2CCF_3)_4(PPh_3)_2$, and $Rh_2(O_2CCF_3)_4(PCy_3)_2$ (class I solution species for the latter two) $J_{AX} = {}^1J_{Rh-P} = 85$ Hz, $J_{AX'} = {}^2J_{Rh-P} = 2$ Hz, $J_{AA'} = J_{Rh-Ph} = 5$ Hz, and $J_{P-P} = J_{XX'} = 300$ Hz and for $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$ $J_{AX} = {}^1J_{Rh-P} = 129.5$ Hz, $J_{AX'} = {}^2J_{rh-P} = 4$ Hz, $J_{AA'} = J_{Rh-}R_h = 7.5$ Hz, and $J_{P-P} = J_{XX'} = 832$ Hz. These values reproduce the observed spectra. The relative magnitudes of the coupling constants are in rough agreement with the accurately determined ones given in ref 9 for $Rh_2(O_2CCH_3)_4(P(OMe)_3)_2$. [b] These J values were determined by using a first-order treatment; simulation of the spectra using an exact treatment showed good agreement. There was an error in the determination of $J_{AB} = J_{Rh-Rh}$. In ref 9, ^{103}Rh NMR measurements were performed on $Rh_2(CO_2CCH_3)_4(P(OMe)_3)_2$ and gave $J_{Rh-Rh} = 7.9$ Hz. Therefore, the approximate value of 8 Hz has been used here.

$- J_{XX'})^2 + (J_{AX} - J_{AX'})^2)^{1/2} \pm |J_{AA'} - J_{XX'}|]$ or $[((J_{AA'} + J_{XX'})^2 + (J_{AX} - J_{AX'})^2)^{1/2} \pm |J_{AA'} + J_{XX'}|]$. An AA′XX′ system has a total of ten lines; however, very often they are not all observed since there can be degeneracies and some lines can be very broad and/or can be of low intensity.[6] Simulation of these AA′XX′ systems is possible but does not give unique solutions. The approximate coupling constants based on simulations are given in Table I. The spectra can be reproduced by assuming a very large P–P coupling through the Rh–Rh bond, but with small $^2J_{Rh-P}$. This is in agreement with the analysis of the $^{31}P\{^1H\}$ NMR spectrum reported[9] for $Rh_2(O_2CCH_3)_4(P(OMe)_3)_2$. This strong coupling through the Rh–Rh bond is not seen in lower oxidation state Rh dimers. For example, in the $^{31}P\{^{19}F\}$ NMR spectra of $Rh_2(PF_3)_8$[7] and the ^{13}C NMR spectrum of ^{13}CO-enriched $(\eta^5\text{-}C_5H_5)_2Rh(\mu\text{-}CO)(CO)_2$[8] coupling to only one Rh nucleus was observed. The Rh(II)–Rh(II) bond allows through-bond interactions not seen in these Rh(I) and Rh(0) species.

The $^{31}P\{^1H\}$ NMR spectrum of $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$ at –50 °C was very similar to that observed for $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$. A single signal was observed at –20 ppm showing the four main peaks expected for an AA′XX′ system, as described above. The outer peaks were separated by 88.3 Hz; the inner peaks, by 10.8 Hz. Thus at –50 °C, only the 2:1 class I adduct is present, with no evidence for other species. However, after the sample warmed to room temperature, the signal became a broad singlet at –19 ppm. This is most likely due to intermolecular PPh_3 exchange. Since the chemical shift change is very small between –50 and +22 °C, the major species is the 2:1 class I adduct, with ligand exchange removing resolution of the coupling effects. These results resemble those reported for $Rh_2(O_2CCH_3)_4(P(OMe)_3)_2$,[9] although this phosphite complex showed signals assignable to 1:1 as well as 2:1 adducts at low temperature. It is clear that, with alkane carboxylate ligands, only axial phosphorus donor coordination occurs in solution as well as in the solid state.

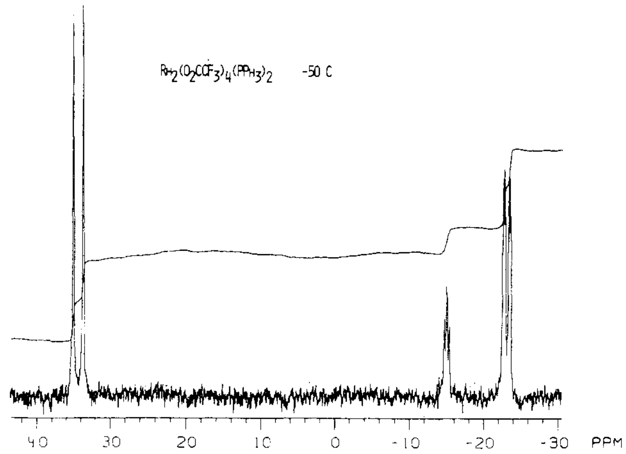

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $Rh_2(O_2CCF_3)_4(PPh_3)_2$ at –50 °C. Expansion of the three signals shows the splitting patterns described in the text.

The situation is quite different for fluoroalkanecarboxylate rhodium dimers with phosphine donors. The $^{31}P\{^1H\}$ NMR spectra of $Rh_2(O_2CCF_3)_4(PPh_3)_2$ and $Rh_2(O_2CCF_3)_4(PCy_3)_2$ were very similar but differed greatly from those of the complexes described above. In our previous study, the $^{31}P\{^1H\}$ NMR spectrum of the PPh_3 adduct appeared to consist of two doublets and a weak triplet.[5] However, resolution and signal-to-noise ratio of this spectrum obtained on a 100-MHz (^{1}H) instrument were not good. A spectrum obtained at 121.5 MHz and at –50 °C on a freshly frozen $CDCl_3$ solution of the pPh_3 adduct revealed the true nature of the splittings. The spectrum is shown in Figure 1. One doublet is actually a doublet of doublets; the other a doublet of quartets. The third signal is a quadruplet that resembles a triplet due to the small splitting of the inner peaks, as was found with the $P(OPh)_3$ adduct. The $^{31}P\{^1H\}$ NMR spectrum of $Rh_2(O_2CCF_3)_4(PCy_3)_2$ (shown in Figure 2), a complex not previously reported, also showed three signals, with chemical shifts and splittings almost identical with those observed for the PPh_3 adduct. (See Table I.) The similarity of the splittings suggests that the solution structures of the two complexes are the same. By analogy with the $P(OPh)_3$ adduct, the weak signal ("triplet") in the spectra of these phosphine complexes most likely corresponds to the class I (axial) adduct. The other two ^{31}P signals most likely arise from a single complex that has a phosphine coordinated axially to one rhodium and equatorially to the other rhodium, a type that we

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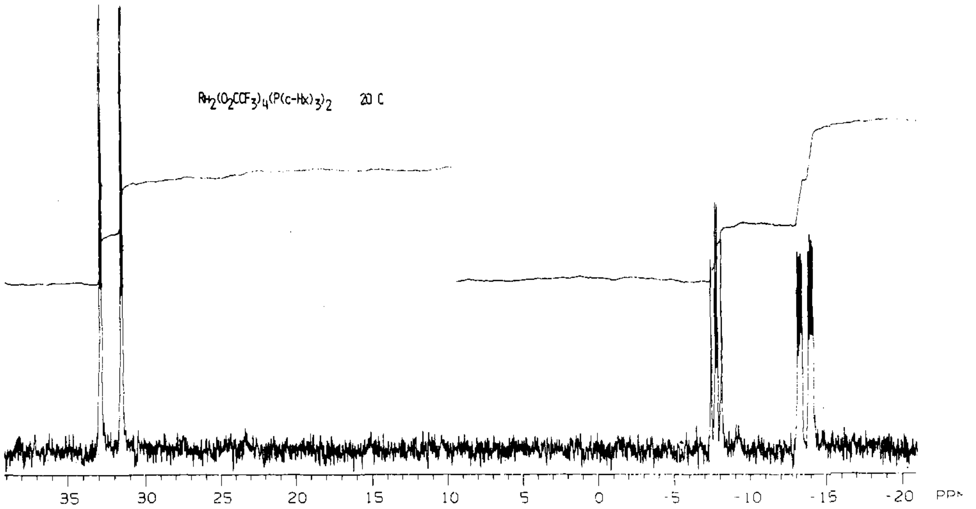

Figure 2. $^{31}P\{^1H\}$ NMR spectrum of $Rh_2(O_2CCF_3)_4(PCy_3)_2$ at 20 °C.

call class III. These two phosphines would not be chemically equivalent and lead to individual signals. By the use of a first-order analysis, the signals are found to correspond to an ABXY spin system (A, B = ^{103}Rh; X, Y = ^{31}P). The coupling constants are given in Table I. The doublet of quartets is due to the axially coordinated phosphine coupled strongly to one rhodium and less strongly to both the other rhodium and the other phosphine. The $^2J_{Rh(eq)-P(ax)}$ value is roughly twice $^3J_{P-P}$ to give the quartet. The doublet of doublets is due to the equatorially coordinated phosphine coupled strongly to one rhodium and weakly to the other phosphine, with coupling to the other rhodium not observed. It is not unreasonable to assume that the axially coordinated phosphine would have a larger $^2J_{Rh-P}$ value than the equatorial phosphine due to coupling along the Rh–Rh bond. It is also possible that both phosphines are coordinated to one Rh atom, although if this were the case, then $^2J_{P-P}$ might be larger. The ^{31}P signals integrated to an area ratio of 2:2:1 in the PCy_3 complex and 3:3:1 in the PPh_3, the last signal corresponding to the axial class I adduct. Since the class I signal represents two equivalent phosphines, the relative ratios in solution of class III to class I adducts are 4:1 for PCy_3 and 6:1 for PPh_3. The greater amount of equatorial coordination with PPh_3 may result from steric effects. It is remarkable that anything other than axial phosphine coordination occurs with either of these bulky, relatively poorly donating phosphines.

The IR and ^{19}F NMR spectra support the class III (axial and equatorial) assignment. As reported previously for $Rh_2(O_2CCF_3)_4(PPh_3)_2$,[5] bands assignable to $\nu_{asy}(CO_2)$ for both mono- and bidentate $CF_3CO_2^-$ are seen for $Rh_2(O_2CCF_3)_4(PCy_3)_2$ in $CDCl_3$ solution at 1710 and 1660 cm^{-1}, respectively. The ^{19}F NMR spectrum of the PCy_3 adduct in $CDCl_3$ at room temperature showed four signals over the range −72 to −76 ppm (relative to $CFCl_3$) with an area ratio of 1:1:2:1. These four signals result from the existence in solution of four chemically different types of coordinated $CF_3CO_2^-$. There are four equivalent $CF_3CO_2^-$ ligands on the class I adduct giving one signal, but there are three types of $CF_3CO_2^-$ on the class III adduct each with a different chemical shift. There are one monodentate and three bidentate $CF_3CO_2^-$ ligands. Two of these are trans to each other and equivalent, the third is trans to the equatorially coordinated phosphine and monodentate $CF_3CO_2^-$. Taking into account the ratio of class III to class I adducts, which was 4:1 for the PCy_3 complex, one obtains a ratio for the four species described above of 1:1:2:1, which was the observed result. Though it is not possible to assign the signals of equal area to specific ligands, the signal farthest downfield is probably due to the monodentate $CF_3CO_2^-$. The ^{19}F spectrum of the PPh_3 adduct in $CDCl_3$ at room temperature contained four major signals. Since the $^{31}P\{^1H\}$ spectrum indicated a 6:1 ratio of class III to class I isomers, the four ^{19}F signals should have an area ratio of 1:1.5:3:1.5, on the basis of the above analysis. Four signals were observed in approximately this area ratio, although several additional, very weak peaks were also seen. This was probably due to decomposition since the solution was not held at low temperature during the ^{19}F spectral accumulation. As will be shown below, the PCy_3 adduct is more stable than the PPh_3 complex.

The occurrence of both axial and equatorial phosphine coordination to $Rh_2(O_2CCF_3)_4$ suggests a mechanism for attack on the Rh–Rh bond leading to monomeric Rh species. Such Rh–Rh bond cleavage was observed with PPh_3, which gave monomeric Rh(I) and Rh(III) complexes.[5] In contrast to the reaction of $Rh_2(O_2CCF_3)_4$ with PPh_3, which gave Rh–Rh bond cleavage in toluene, only the brown axial adduct $Rh_2(O_2CCF_3)_4(PCy_3)_2$ was obtained even with 10 equiv of PCy_3 in toluene, CH_2Cl_2, and THF solvents. Tricyclohexylphosphine has poorer π-acceptor properties than PPh_3 and is also more bulky. These properties lead to the larger amount of class I adduct in solution and to greater resistance toward Rh–Rh bond cleavage by excess phosphine. However, reaction of $Rh_2(O_2CCF_3)_4$ with excess PCy_3 in both 1:1 toluene/acetonitrile and 1:1 THF/acetonitrile solvents readily gave a pale yellow complex. The yellow color is observed for both Rh(I) and Rh(III) complexes such as $RhCl(PCy_3)_2$ and $RhH_2Cl(PCy_3)_2$.[11] Elemental analysis indicated that the yellow complex is most likely primarily $Rh(O_2CCF_3)(PCy_3)(CH_3CN)$. IR data indicated mono- and bidentate $CF_3CO_2^-$ and end-on coordinated acetonitrile (see Experimental Section). The product is probably contaminated with a variety of other species as well as unreacted and/or oxidized phosphine. PPh_3 oxidation was observed earlier,[5] and PCy_3 is much more easily oxidized. An interesting possibility is that Rh–Rh bond cleavage would occur to give monomeric Rh(II) species. These might be stabilized by PCy_3, since one of the very few reported[10] monomeric Rh(II) complexes is $RhCl_2(PCy_3)_2$, a blue, EPR-active complex. It is possible that $Rh(O_2CCF_3)_2(PCy_3)_2$ is present in a very small amount, since a very weak but distinct EPR signal was observed for the reaction product in CH_2Cl_2 at 77 K. The EPR spectrum appeared to be roughly axial with a perpendicular signal at $g = 2.01$ and a very weak parallel signal at $g = 2.12$. Some hyperfine splitting presumably from Rh and/or P was also observed. Thus, it appears that a Rh(II) species is present, but in very low concentration. It would be of great interest to determine whether Rh–Rh bond cleavage occurs via formation of monomeric Rh(II) complexes that rapidly disproportionate or if Rh(I) and Rh(III) complexes are formed directly from heterolytic cleavage of the metal–metal bond. This process is an interesting one, since phosphines attack one end of the dimer and displace a carboxylate bridge. The rhodium retaining $CF_3CO_2^-$ becomes Rh(III) while the rhodium with the most extensive phosphine coordination receives the metal–metal-bonding electrons and becomes Rh(I).

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Support for this proposal is suggested by the reaction of $Rh_2(O_2CCF_3)_4$ with excess $P(OMe)_3$. This reaction was studied earlier, but difficulties in obtaining good NMR spectra were encountered. The reaction of $Rh_2(O_2CCF_3)_4$ with 10 equiv of $P(OMe)_3$ yields a pale yellow solid of empirical formula $Rh(O_2CCF_3)_2(P(OMe)_3)_3$. However, we suggested[5] that the complex was most likely $Rh(P(OMe)_3)_4{}^+Rh(O_2CCF_3)_4(P(OMe)_3)_2{}^-$, four-coordinate Rh(I) and six-coordinate Rh(III) species, respectively. The previously reported $^{31}P\{^1H\}$ and ^{19}F NMR spectra of this species were more complex than expected. This was probably due to interconversion between Rh complexes over time while in solution at room temperature. In this study, a $CDCl_3$ solution of the $P(OMe)_3$ complex was frozen at −70 °C and held at that temperature except when NMR spectra were obtained. The $^{31}P\{^1H\}$ NMR spectrum obtained in this manner showed two sharp doublets in a 2:1 area ratio over the temperature range −50 to +20 °C. No significant changes in either chemical shift or coupling constants were seen. The signals appeared at 135.0 ± 0.5 ppm (relative to 85% H_3PO_4), $J = 181.5 \pm 0.1$ Hz, and at 89.5 ± 0.5 ppm, $J = 132.5 \pm 0.5$ Hz. The ^{19}F spectrum showed a single sharp peak at −75.33 ppm at room temperature. $Rh(O_2CCF_3)_4(P(OMe)_3)_2{}^-$ is an AX_2 spin system as the trans isomer, showing a doublet in the X region, and would show a single ^{19}F signal for four equivalent monodentate $CF_3CO_2{}^-$ ligands (IR $\nu_{asy}(CO_2)$ at 1720 cm^{-1} in $CHCl_3$). $Rh(P(OMe)_3)_4{}^+$ is an AX_4 spin system and also shows a ^{31}P doublet. Over time, and probably as a result of O_2 and/or light, other Rh species could come about. The chemistry of transition-metal phosphite complexes is complicated, and a variety of species are known for cobalt[12] and other metals.[13] For rhodium, $Rh(P(OMe)_3)_5{}^+$ and $Rh(OP(OMe)_2)(P(OMe)_3)_4$ have been reported.[14,15] In the system reported here, the Rh–Rh bond in $Rh_2(O_2CCF_3)_4$ probably is cleaved asymmetrically by $P(OMe)_3$ to give a phosphite-coordinated Rh(I) species and a Rh(III) species containing all the $CF_3CO_2{}^-$ ligands. This type of reaction also occurs with phosphines, although oxidation to phosphine oxides complicates matters. Somehow asymmetric phosphorus donor coordination to the rhodium dimer polarizes the Rh–Rh bond and cleaves carboxylate bridges leading to formation of Rh(I) complexes that coordinate only the phosphorus donors and Rh(III) complexes that coordinate two phosphines and the $CF_3CO_2{}^-$ ions.

Experimental Section

$Rh_2(O_2CCF_3)_4$, $Rh_2(O_2CCF_3)_4(PPh_3)_2$, $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$, $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$, and $Rh(O_2CCF_3)_2(P(OMe)_3)_3$ were synthesized as described previously.[5] $Rh_2(O_2CCF_3)_4(PCy_3)_2$ was prepared by dropwise addition of a toluene solution of PCy_3 (2 equiv, Aldrich) to a toluene solution of $Rh_2(O_2CCF_3)_4$. Removal of solvent by pumping and recrystallization from toluene gave brown $Rh_2(O_2CCF_3)_4(PCy_3)_2$. IR ($cm^{-1}$): $\nu_{asy}(CO_2)$ 1663 (Nujol), 1710 w, 1660 m ($CHCl_3$). ^{19}F NMR ($CDCl_3$, 27 C, ppm relative to $CFCl_3$): −72.73, −74.51, −75.42, −75.92 (1:1:2:1). Anal. Calcd for $Rh_2C_{44}H_{66}P_2F_{12}O_8$: C, 43.36; H, 5.46; P, 5.08. Found: C, 45.53; H, 5.49; P, 5.23. Following the above procedure but using excess PCy_3 (10 equiv) and $Rh_2(O_2CCF_3)_4$ in 1:1 toluene/acetonitrile led to a solution color change from brown to pale yellow after heating at 40 °C for 30 min. Removal of solvent by pumping and recrystallization from 1:1 CH_2Cl_2/hexane afforded a pale yellow solid. IR (cm^{-1}, Nujol): $\nu(CN)$ 2260 m; $\nu_{asy}(CO_2)$ 1735 s, 1680 s; $\nu(CF_3)$ 1180 s, 1140 s; $\delta(CO_2)$ 725 s. Anal. Calcd for $Rh(O_2CCF_3)(P(C_6H_{11})_3)(CH_3CN)$: C, 49.17; H, 6.75; N, 2.61; P, 5.76; C:H:N:P = 22:36:1:1. Found: C, 53.69; H, 7.40; N, 2.84: P, 6.50; C:H:N:P = 22.0:36.2:1.0:1.0. The product is contaminated with PCy_3 and complexes thereof, giving the high % C, % H, and % P.

NMR spectra were recorded on a Nicolet NT-300 instrument operating at a field of 7 T. $^{31}P\{^1H\}$ (121.5 MHz) sample were in $CDCl_3$ in 5-mm tubes coaxial in 12-mm tubes, the latter containing $P(OMe)_3$ in $CDCl_3$ as an external chemical shift reference (140.0 ppm relative to 85% H_3PO_4). ^{19}F (282.3 MHz) samples were in 5-mm tubes containing $CFCl_3$ as an internal reference.

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Registry No. $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$, 90968-08-4; $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$, 77966-17-7; $Rh_2(O_2CCF_3)_4(PPh_3)_2$ (class I), 77966-16-6; $Rh_2(O_2CCF_3)_4(PPh_3)_2$ (class III), 102745-66-4; $Rh_2(O_2CCF_3)_4(PCy_3)_2$ (class I), 83398-63-4; $Rh_2(O_2CCF_3)_4(PCy_3)_2$ (class III), 102745-67-5; $[Rh(O_2CCF_3)_4[P(OMe)_3]_2]^-[Rh(P(OMe)_3)_4]^+$, 102745-69-7; $Rh(O_2CCF_3)(P(C_6H_{11})_3)(CH_3CN)$, 102745-70-0; $Rh_2(O_2CCF_3)_4$, 31126-95-1.

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Small Macrocyclic Ligands with Mixed Nitrogen- and Oxygen-Donor Atoms

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The stability of some of the complexes of the metal ions Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ca^{2+}, and Hg^{2+} with the ligands 9-aneN_2O (1-oxa-4,7-diazacyclononane), 12-aneN_3O (1-oxa-4,7,10-triazacyclododecane), 12-ane(1,4)N_2O_2 (1,4-dioxa-7,10-diazacyclododecane), 13-aneN_3O (1-oxa-4,7,11-triazacyclotridecane), 13-aneN_2O_2 (1,4-dioxa-7,11-diazacyclotridecane), HEEN (1-oxa-4,7-diazaheptane), ODEN (4-oxa-1,7-diazaheptane), DHEEN (1,10-dioxa-4,7-diazadecane), and 12-aneN_4 (1,4,7,10-tetraazacyclododecane) are reported. It is shown that addition of neutral oxygen donors to existing amine ligands leads to an increase in complex stability for large metal ions (e.g. Pb^{2+}, Ca^{2+}) and a decrease for small metal ions (e.g. Cu^{2+}, Zn^{2+}). This occurs whether the added oxygen donors are part of hydroxyalkyl groups, as in the addition of hydroxyethyl groups to en (ethylenediamine) to give DHEEN or the addition of ethereal oxygens that are part of a macrocyclic ring to en to give 12-ane(1,4)N_2O_2. It is found that the macrocyclic effect in mixed-donor ligands is much smaller than in the all-nitrogen-donor analogues. Thus, the increase in complex stability (the macrocyclic effect) in passing from DHEEN to 12-aneN_2O_2, for example, is much smaller than in passing from TRIEN (1,4,7,10-tetraazadecane) to 12-aneN_4. This is discussed in terms of ligand-related contributions to the macrocyclic effect, such as steric hindrance to the solvation of the free ligand. A feature of these ligand-related effects is that a metal ion such as Ca^{2+}, which ordinarily shows little affinity for ligands containing only nitrogen donors, will still form a complex of some stability with a ligand such as 12-aneN_4, with log K_1 at 25 °C in 0.1 M $NaNO_3$ of 3.1.

An interesting feature of macrocyclic chemistry is the fact that the oxygen-donor macrocycles complex strongly only with the alkali- and alkaline-earth-metal ions, plus a few large metal ions such as Pb^{2+} and Hg^{2+}. In contrast, the nitrogen-donor macrocycles appear to complex well only with the transition-metal and post-transition-metal ions, such as Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, or Cd^{2+}. A few metal ions such as Pb^{2+} and Hg^{2+} appear able to bond well to both classes of macrocycle. An obvious area for investigation

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