Inorg. Chem. **1984**, *23*, 2599-2606

axial and equatorial positions: Δd(Ni–Cl) = 0.04 Å and Δd(Ni–N) = 0.088 Å. The contribution of bond rearrangement to the intrinsic factors in electron transfer is well-known. The Ni(II/III) exchange involves the transfer of a dσ^* electron between the high-spin d^8 Ni(II) and the low-spin d^7 Ni(III). The relatively small changes in the bond length, especially for the Ni–Cl bonds, may favor a more rapid electron transfer. Unfortunately there are at present very few well-characterized Ni(II/III) couples that retain octahedral symmetry. The exchange rate for $Ni(nonaneN_3)_2^{3+/2+}$ has been determined[17] as 6×10^3 M^{-1} s^{-1}. In the $Ni(bpy)_3^{2+/3+}$ system, where bond extensions are believed to be of the order of ~0.1 Å, $k_{11} \simeq 2 \times 10^3$ M^{-1} s^{-1}. (In the hexadentate Ni(IV/III) oxime system, where Δd(Ni–N) values are similar, $k_{11} \approx 6 \times 10^4$ M^{-1} s^{-1}).

Although Ti(III) in chloride media is known to reduce oximes to imines,[37] which are further hydrolyzed to carbonyls

$$>NOH \xrightarrow{Ti(III)} >NH \xrightarrow{H_2O} >O$$

there is no evidence of any reaction of this type with the coordinated oxime.

Conclusion

Evidence has been presented for an outer-sphere mechanism in the reduction of various nickel(III) (and one Ni(IV)) complexes by Ti(III). Estimates have been made of the self-exchange rates of $NiLCl_2^{+/0}$ couples (L = saturated macrocycle), and despite a large driving force for these reactions adherence is observed with the Marcus correlation.

Acknowledgment. We thank NSERC (Canada) and the University of Victoria for support. O.O. acknowledges support for study leave from the University of Ife. Dr. Paul Norman is thanked for providing a sample of $Ni(nonane)_2(ClO_4)_3$ and for helpful discussions.

Registry No. Ti, 7440-32-6; $Ni(cyclam)^{3+}$, 72360-42-0; $Ni(Me_2cyclam)^{3+}$, 90413-06-2; $Ni(oxime)^{2+}$, 55188-33-5; $Ni(nonaneN_3)_2^{3+}$, 90413-07-3; Ni(tet-*c*)$^{3+}$, 79329-59-2; $Ni(Me_2diene)^{3+}$, 90413-08-4; $Ni(cyclam)Cl_2^+$, 60105-34-2; $Ni(Me_2cyclam)Cl_2^+$, 90413-09-5.

Supplementary Material Available: Tables of rate constants giving details of hydrogen ion and other concentration dependences (8 pages). Ordering information is given on any current masthead page.

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Reactions of Rhodium Trifluoroacetate with Various Lewis Bases. Formation of 4:1 Complexes with Pyridine and *tert*-Butyl Isocyanide and Rhodium–Rhodium Bond Cleavage with Phosphorus Donors

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The title compound was reacted with Lewis bases tetrahydrofuran (THF), dimethyl sulfoxide (Me_2SO), *N,N*-dimethylformamide (DMF), piperidine, pyridine, *N*-methylimidazole, acetonitrile, *tert*-butyl isocyanide, triphenylphosphine, triphenyl phosphite, dimethylphenylphosphine, and trimethyl phosphite. With THF, Me_2SO, acetonitrile, and $P(OPh)_3$, adducts were formed with axial ligands in analogy to previously reported $Rh_2(O_2CR)_4L_2$ complexes. However, for the other nitrogen donors and isocyanide, equatorial adduct formation occurred in solution followed in the case of piperidine and *N*-methylimidazole by decomposition. With pyridine and *t*-BuNC, 4:1 adducts were isolated constituting a new type of metal–metal bonded complex. Reaction with PMe_2Ph, PPh_3, and $P(OMe)_3$ resulted in dimer cleavage to give monomeric Rh(I) and Rh(III) products that were isolated for the latter two bases. IR and ^{19}F, ^1H, and ^{31}P NMR spectroscopies were used to characterize the complexes. These methods can distinguish between mono- and bidentate $CF_3CO_2^-$ coordination. Comparison with earlier studies of the $Mo_2(O_2CCF_3)_4$ and $Rh_2(O_2CCH_3)_4$ systems shows the changes in reactivity that occur when the metals or carboxylate ligands are changed in these metal carboxylate dimers. Phosphorus donors do not cleave the Mo–Mo bond in $Mo_2(O_2CCF_3)_4$. Only 2:1 axial adducts with pyridine, *t*-BuNC, and $P(OMe)_3$ are formed with $Rh_2(O_2CCH_3)_4$.

Introduction

Metal carboxylate dimers have been widely studied.[1] These systems are of interest since they provide excellent models to study metal synergism. Because of the wide variety of metals that form metal carboxylate dimers, the chemistry of the metal–metal bond can be probed as a function of the d-electron population. One area in which a synergistic influence from metal–metal bonding has been established is in the affinity of the metal dimer for Lewis bases. In previous studies from this laboratory,[2] the coordination of ligands to the termini of the metal–metal axis in the $Rh_2(O_2CR)_4$ and $Mo_2(O_2CR)_4$ systems was studied. The metal–metal interaction in the dirhodium complex was found to lead to a very effective metal to ligand π-back-bonding interaction. Variation in the bridging carboxylate was also shown to have an effect on the metal–ligand bond strength. The comparison of the rhodium to the molybdenum system is of particular interest since in $Mo_2(O_2CR)_4$ a quadruple bond exists while in $Rh_2(O_2CR)_4$ there is a single bond.[3-5] In the rhodium system, the LUMO is the σ^* orbital and the filled π^* plays an important role in the chemistry of this system.[2] With a stronger metal–metal in-

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Table I. ^{19}F NMR Data for $Rh_2(O_2CCF_3)_4$ Complexes[a]

complex	^{19}F chem shift[b]	area ratios	solvent	temp, °C
$Rh_2(O_2CCF_3)_4$	−73.28		CD_3NO_2	−35
	−74.29		toluene-d_8	−60
	−75.04		toluene-d_8	+27
$Rh_2(O_2CCF_3)_4(THF)_2$	−74.65		$CDCl_3$	−50
	−75.19		$CDCl_3$	+27
$Rh_2(O_2CCF_3)_4(Me_2SO)_2$	−74.17		$CDCl_3$	−60
	−76.41		$CDCl_3$	+27
$Rh_2(O_2CCF_3)_4(DMF)_2$	−74.18		$CDCl_3$	−60
	−74.86		$CDCl_3$	+27
$Rh_2(O_2CCF_3)_4(Et_3N)_2$	−75.31		$CDCl_3$	−40
	−75.92		$CDCl_3$	+27
$Rh_2(O_2CCF_3)_4(py)_4$	−74.69, −75.44	1:1	$CDCl_3$	−60
	−74.08, −74.87	1:1	toluene-d_8	−60
	−74.73, −75.34	1:1	toluene-d_8	+27
$Rh_2(O_2CCF_3)_4$(*t*-BuNC)$_4$	−73.0, −73.2, −73.4, −73.8, −74.2, −74.6	2:1:1.5:4:1.5:1	$CDCl_3$	−60
$Rh_2(O_2CCF_3)_4(PPh_3)_3$	−73.98, −74.90 (−75.23),[c] −75.72	1:1:1.3	$CDCl_3$	−50
	−74.41, −74.75 (−75.32),[c] −75.88	1:1:2.0	$CDCl_3$	+27
$Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$	−75.08		$CDCl_3$	+27
	−74.68, −74.83 (−75.10, −75.45, −76.20)[c]	2.5:1	$CDCl_3$	−50
$Rh(O_2CCF_3)_2(P(OMe)_3)_3$	−73.40, −73.88	3:2	$CDCl_3$	−50
	−74.65, −75.25	3:2	$CDCl_3$	+27

[a] Data are reported for those complexes that were obtainable as genuine adducts and the $P(OMe)_3$ complex. Solution studies were undertaken on other systems and are described in the text. [b] All chemical shifts are given in ppm with respect to internal $CFCl_3$. [c] These signals are of very low intensity and may indicate the beginning of complex decomposition.

teraction in the dimolybdenum system than in that of dirhodium, the σ^* orbital is higher in energy and the molybdenum system is a much poorer Lewis acid than rhodium in regard to coordination to this axial site. This conclusion resulted from a thermodynamic study of Lewis base adduct formation by these two metal systems.[2d]

Andersen and co-workers have synthesized and characterized a number of adducts of molybdenum trifluoroacetate with phosphines and other Lewis bases.[6,7] They found that $Mo_2(O_2CCF_3)_4$ not only forms adducts in which there is coordination along the Mo–Mo axis but also forms some in which there is coordination in sites perpendicular to the Mo–Mo axis. All these complexes are of general formula $Mo_2(O_2CCF_3)_4L_2$. Those with axial coordination are called class I adducts, and those with equatorial coordination, class II. Only Lewis bases that are sterically small and good σ donors are reported[6] to give isolable equatorial adducts. Examples are PMe_3, PEt_3, and PMe_2Ph. Andersen estimated steric bulk by cone angle[8] and σ donor strength by ν(CO) values. The assignment of complexes into the two classes was made on the basis of ^{19}F and ^{31}P NMR spectroscopy, which showed different signals corresponding to phosphines in different coordination sites. Infrared spectroscopy also showed different $\nu(CO_2)$ for the two types of CF_3CO_2 ligands. However, some controversy exists over the assignment of IR and NMR peaks observed for these types of complexes. Cotton and Lay[9] also prepared phosphine complexes of $Mo_2(O_2CCF_3)_4$ and obtained spectra at variance with those of Andersen and co-workers.[6] In addition, these two groups reported different structures for the complex $Mo_2(O_2CCF_3)_4(PMePh_2)_2$. Cotton and Lay[9] obtained a class II (equatorial) adduct, and Andersen,[7] a class I (axial) adduct. Slight variations in synthetic procedure led to this difference since $PMePh_2$ is a phosphine intermediate on the size and donor strength scales.[6,7]

We decided to carry out studies on the $Rh_2(O_2CCF_3)_4$ system for several reasons. We were interested in comparing the reactivity of the metal–metal single bond in $Rh_2(O_2CCF_3)_4$ with the quadruply bonded molybdenum analogue. We also hoped our studies would shed some light on the discrepancies in the spectroscopic properties and interpretations of the systems that were mentioned previously. Finally, although $Mo_2(O_2CCF_3)_4$ complexes have been studied extensively in solution[6,9,10,11] and crystallographically,[7,9,24] the analogous rhodium system has not been studied as extensively,[1] particularly in solution. Crystal structures[12,16] have been determined for several adducts of general formula $Rh_2(O_2CR)_4L_2$. More relevant to this study, crystal structures have been determined where R = CF_3 and L = Me_2SO,[16] Me_2SO-d_6,[17] PPh_3,[18] $P(OPh)_3$,[18] and EtOH.[19] In all these cases, with alkyl and fluoroalkyl carboxylates, only class I (axial) adducts were found. With bridging fluoroacetate ligands, the strongly electron-withdrawing nature of the CF_3 group should enhance the Lewis acidity of the metal dimer[2] and may enhance displacement of a carboxylate oxygen by base, leading to monodentate coordination.[6] We find that the use of this bridging ligand leads to isolation of Lewis base adducts in which there is monodentate fluoroacetate. The results of these studies using a variety of Lewis bases are discussed below.

Results and Discussion

The ^{19}F NMR spectrum of $Rh_2(O_2CCF_3)_4$ was obtained in both CD_3NO_2 and toluene-d_8. (NMR data are summarized in Table I.) Nitromethane and toluene are very weak bases, and thus both should coordinate weakly, if at all, to the rhodium dimer. We find a sharp singlet at both room and low temperatures in both solvents corresponding to the four equivalent bridging fluoroacetates. What is significant is that these signals occur in the −73 to −75 ppm (relative to internal $CFCl_3$) range (they are somewhat solvent and temperature

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Table II. Infrared Data for $Rh_2(O_2CCF_3)_4$ Complexes

complex	$\nu_{asy}(CO_2)$,[a] cm^{-1}	
	$CHCl_3$ solution	Nujol mull
$Rh_2(O_2CCF_3)_4$	1670	1650
$Rh_2(O_2CCF_3)_4(THF)_2$	1658	1668
$Rh_2(O_2CCF_3)_4(Me_2SO)_2$	1655	1662
$Rh_2(O_2CCF_3)_4(DMF)_2$	1662	1650 br[b]
$Rh_2(O_2CCF_3)(Et_3N)_2$	1670 s, 1660 s	1660 s, 1650 s
$Rh_2(O_2CCF_3)_4(py)_4$	1705 s, 1642 m	1705 s, 1655 s
$Rh_2(O_2CCF_3)_4$(*t*-BuNC)$_4$	1693 s br, 1658 s	1720 m br, 1660 m br
$Rh_2(O_2CCF_3)_4(PPh_3)_2$	1715 w, 1654 m, 1652 m	1665
$Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$	1665	1670
$Rh_2(O_2CCH_2CH_2CH_3)_4$-$(PPh_3)_2$[c]	1587	
$Rh_2(O_2CCF_3)_4(CH_3CN)_2$	1658 m, 1648 w	1663 m, 1653 w

[a] s = strong, m = medium, w = weak, br = broad. [b] Includes amide ν(CO), resolved in solution. [c] Included to contrast with $Rh_2(O_2CCF_3)_4(PPh_3)_2$.

dependent). Earlier workers[6,10,11] have assigned peaks in the −72 to −74 ppm region to monodentate $CF_3CO_2^-$ and peaks at −70 ppm to bidentate $CF_3CO_2^-$ in $Mo_2(O_2CCF_3)_4$ complexes. The IR spectrum of $Rh_2(O_2CCF_3)_4$ shows a single $\nu_{asy}(CO_2)$ in solution and in the solid state. (IR data are summarized in Table II). However, this stretch occurs at a higher frequency (1650–1670 cm^{-1}) than $\nu_{asy}(CO)_2$ for bidentate $CF_3CO_2^-$ in the molybdenum systems (ca. 1600 cm^{-1}). Thus, there is no direct correspondence between the location of ^{19}F NMR and IR bands for the rhodium and molybdenum systems. Nevertheless, mono- and bidentate $CF_3CO_2^-$ give significantly different spectra in the rhodium complexes (vide infra).

Oxygen Donors. Emerald green $Rh_2(O_2CCF_3)_4$ forms blue 2:1 complexes with oxygen donor bases such as THF, Me_2SO, and DMF. The THF adduct is stable, but heating at 100 °C under vacuum effects quantitative removal of THF to give the base-free starting material. The ^{19}F NMR and IR spectra of this complex are characteristic of a class I adduct. A singlet is observed in the ^{19}F NMR spectrum at −75 ppm, and $\nu(CO_2)$ occurs at about 1660 cm^{-1} in both the solid adduct and in solution. These results are similar to those for the free acid, $Rh_2(O_2CCF_3)_4$. The crystal structure of $Rh_2(O_2CCF_3)_4(Me_2SO)_2$ shows a typical class I adduct,[16] and there is nothing in the ^{19}F NMR spectrum to indicate otherwise in solution since a single peak is observed. The IR spectrum shows a single $\nu_{asy}(CO_2)$ at 1662 cm^{-1} (Nujol mull) in agreement with the an axial adduct. A doublet at 945 (s) and 937 (s) cm^{-1} (Nujol mull) and one at 948 (m) and 931 (w) cm^{-1} ($CHCl_3$ solution) are observed corresponding to ν(SO) of O-bound Me_2SO. No bands occur in the 1050–1150-cm^{-1} region where S-bound Me_2SO would absorb.[16] When DMF is added to $Rh_2(O_2CCF_3)_4$, a purple color appears and the solution then rapidly turns dark blue. The ^{19}F NMR spectrum of this complex shows a single peak at −74 ppm at room and low temperatures. Addition of excess DMF does not change the spectrum. This is in contrast to Me_2SO. Kitchens and Bear[20,21] report that addition of excess Me_2SO to $Rh_2(O_2CCF_3)_4$ leads to formation of a yellow decomposition product. $Rh_2(O_2CCF_3)_4$ remains intact as a 2:1 class I adduct in excess DMF and forms a stable solid adduct. The IR spectrum is also characteristic of a class I adduct ($\nu_{asy}(CO_2)$ at 1662 cm^{-1}, $CHCl_3$ solution). In solution the amide ν(CO) could be resolved from the $\nu_{asy}(CO_2)$ (this was not possible in the solid) and was shifted from 1667 cm^{-1} in the free base to 1643 cm^{-1} in the adduct, indicative of O-coordination.

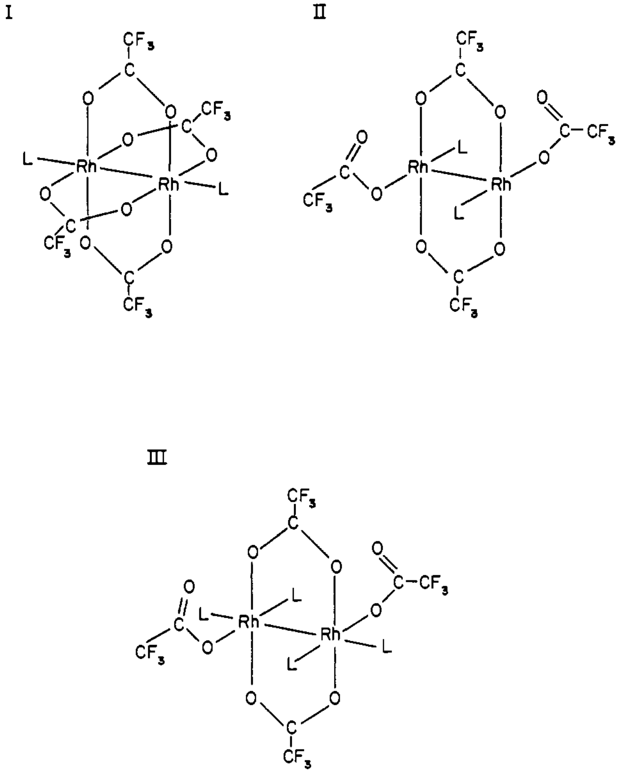

Figure 1. Types of ligand coordination to $Mo_2(O_2CCF_3)_4$. Only one of the six isomers of class II and III adducts is shown.

Nitrogen Donors. A variety of nitrogen donor bases were reacted with $Rh_2(O_2CCF_3)_4$ with varying results. Isolable, analytically pure adducts were not obtained with piperidine and *N*-methylimidazole. When these bases are added to toluene solutions of $Rh_2(O_2CCF_3)_4$, a red color immediately results, indicative of nitrogen base coordination. However, after several hours the solution turns yellow and evaporation gives an intractable yellow tar in both cases, indicative of dimer cleavage.[21] Some ^{19}F NMR studies were performed on solutions of $Rh_2(O_2CCF_3)_4$ and these bases. A freshly prepared solution containing 10:1 *N*-methylimidazole:$Rh_2(O_2CCF_3)_4$ showed single peaks at −74.6 ppm at 27 °C and at −74.1 ppm at −61 °C in $CDCl_3$. Thus, a 2:1 axial adduct forms initially; it lasts only a few hours, for a yellow color then appears, and the spectrum becomes complex. A freshly prepared solution of 10:1 piperidine:$Rh_2(O_2CCF_3)_4$ exhibited a major peak at −74.2 ppm and smaller peaks at −68.4 and −80.3 ppm at −60 °C in toluene-d_8, indicating that rapid decomposition occurs. The major peak is presumably from axially coordinated dimer. The other two peaks correspond to decomposition products. Adducts with these two bases might be prepared if excess base were not present. By contrast, use of excess triethylamine led to facile isolation of $Rh_2(O_2CCF_3)_4(Et_3N)_2$. This complex has an IR spectrum characteristic of bidentate $CF_3CO_2^-$ in solution and in the solid state (see Table II). The ^{19}F NMR spectrum shows a single peak at −75 ppm at room and low temperatures (see Table I). With pyridine, an interesting product is formed that is intermediate between the class I adduct formed with Et_3N and the decomposition product of piperidine and *N*-methylimidazole. This complex is a stable red 4:1 adduct containing both axially (class I) and equatorially (class II) coordinated Lewis bases and thus may be considered a new type of product that we call class III (see Figure 1). Contrast this behavior to the reaction of pyridine with $Mo_2(O_2CCF_3)_4$[23]

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and $Rh_2(O_2CCH_3)_4$[12] in which class I adducts form. A precendent for this class III compound exists. Webb and Dong[20] have performed solution studies on $Mo_2(O_2CCF_3)_4$ with varying amounts of pyridine and found ^{19}F NMR signals in the places predicted[6] for mono- and bidentate $CF_3CO_2^-$ (−70.5, −75.3 ppm) and IR absorption bands at 1713, 1617, and 1611 cm^{-1} corresponding to $\nu_{asy}(CO_2)$ of mono- and bidentate $CF_3CO_2^-$. Only one Mo–Mo stretch was observed in the Raman spectrum (343 cm^{-1}), indicating the presence of only one centrosymmetric isomer. We find at −60 °C for $Rh_2(O_2CCF_3)_4(py)_4$ ^{19}F NMR signals at −74.1 and −74.9 ppm in toluene-d_8 and −74.7 and −75.4 ppm in $CDCl_3$. In both solvents the peak ratio is 1:1. Mono- and bidentate $CF_3CO_2^-$ resonances are separated by less than 1 ppm whereas in the molybdenum work[6,10] they are separated by ca. 3 ppm. There are examples of mono- and bidentate $CF_3CO_2^-$ with resonances in the −74 to −76 ppm range. King and Kapoor[24] have synthesized a large number of compounds such as $(CF_3CO_2)Fe(CO)_2(C_5H_5)$ with monodentate $CF_3CO_2^-$, giving a ^{19}F NMR signal at −74.2 ppm in $CDCl_3$. Creswell and coworkers[25] have prepared compounds such as $Os(O_2CCF_3)_2(CO)(PPh_3)_2$, which has two ^{19}F NMR signals at −75.44 and −75.22 ppm in $CDCl_3$ assigned to mono- and bidentate $CF_3CO_2^-$. Thus, the locations of resonances in the rhodium dimer differ from those of molybdenum, and the chemical shift differences between $CF_3CO_2^-$'s in different environments do not correspond. The IR data on the pyridine complex are also in agreement with the class III formulation. Absorption bands for $\nu_{asy}(CO_2)$ are observed at 1705 and 1642 cm^{-1} ($CHCl_3$ solution) and 1705 and 1655 cm^{-1} (Nujol mull) corresponding to mono- and bidentate $CF_3CO_2^-$. The other absorption bands can be assigned to either pyridine or $Rh_2(O_2CCF_3)_4$, and the latter show little change from base-free rhodium dimer. Addition of excess pyridine, up to 20 equiv, causes no change in the ^{19}F NMR spectrum. Two sharp peaks of equal intensity are still observed at −74.7 and −75.3 ppm in toluene-d_8 at 27 °C. By contrast, in the molybdenum case the two peaks coalesce at 30 °C, indicating fast exchange. However, the slower exchange observed here is not unusual since in the $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$ complexes studied by Creswell and co-workers[25] separate resonances corresponding to mono- and bidentate $CF_3CO_2^-$ were observed at room temperature. As a final note, it should be mentioned that the synthesis of "$Rh_2(O_2CCF_3)_4(py)_2$" was reported a number of years ago[26] but characterized only by C and H analysis. We repeated this work and isolated a compound that is most likely a mixture of pyridine adducts resulting from the use of ethanol rather than toluene as solvent, (see Experimental Section).

It is difficult to draw general conclusions from the above results based on criteria such as size and σ donor and π acceptor abilities of the bases. Triethylamine is the strongest σ donor studied; it is bulky and has no π acceptor abilities. It forms axial adducts. Similarly, quinuclidine (a base very comparable to Et_3N) forms a class I (axial) adduct with $Mo_2(O_2CCF_3)_4$ although its size and basicity would favor class II.[6] Pyridine, a base with less σ donor ability than Et_3N, has π acceptor ability and forms a stable class II adduct (axial and equatorial). *N*-Methylimidazole, a stronger σ donor but a poorer π acceptor than pyridine causes dimer cleavage although via a class I adduct. Piperidine is a strong σ donor, but reactivity is most likely due to the protonic nature of the base. A final nitrogen donor base, acetonitrile, was used. It is a weak σ donor, but a π-acceptor. Das, Kadish, and Bear[22] were unable to isolate a stable acetonitrile adduct of $Rh_2(O_2CCH_2CH_3)_4$. Evaporation of a CH_3CN solution of the rhodium dimer gave only starting material.[22] We find, by contrast, that purple $Rh_2(O_2CCH_3)_4(CH_3CN)_2$ is formed upon evaporation of a CH_3CN solution of rhodium acetate (see Experimental Section). Although $Rh_2(O_2CCF_3)_4(CH_3CN)_2$ can be synthesized, it is readily hydrated to a blue-green material on standing. ^{19}F NMR spectroscopy of the acetonitrile complex showed a singlet at −74.1 ppm and a doublet at −74.5 ppm at −60 °C in $CDCl_3$ in area ratios of 2:1:1. Addition of excess CH_3CN (approximately 10 equiv) leads to signals at −74.7 and −75.4 ppm in equal area ratios. IR data showed class I bridging $CF_3CO_2^-$ (Table I) for the acetonitrile system.

Isocyanide. The reaction of *t*-BuNC with a variety of metal carboxylate dimers[27] showed that only monomeric complexes were obtained with $Mo_2(O_2CCH_3)_4$, $Mo_2(O_2CCF_3)_4$, $Re_2(O_2CCH_3)_4Cl_2$, and $Ru_2(O_2CCH_3)_4Cl$. However, with $Rh_2(O_2CCH_3)_4$ only the class I adduct $Rh_2(O_2CCH_3)_4(t\text{-}BuNC)_2$ was obtained. We were interested in the effect replacement of $CH_3CO_2^-$ by $CF_3CO_2^-$ would have in the dirhodium system. We find that reaction of $Rh_2(O_2CCF_3)_4$ with excess *t*-BuNC leads to isolation of an air-stable orange-brown complex best formulated as $Rh_2(O_2CCF_3)_4(t\text{-}BuNC)_4$. Unfortunately, in contrast to the pyridine compound, which has the same stoichiometry and easily interpretable NMR and IR spectra, *t*-BuNC gave complicated results (vide infra). This is due to a variety of species being present in solution including more than one isomer of a class III adduct and possibly monomeric species. Although *t*-BuNC and pyridine have similar σ donor properties,[27] *t*-BuNC is a better π acceptor and somehow this may lead to a variety of isomers of comparable stability. The ^{19}F NMR spectrum of this compound shows six peaks occurring between −73.0 and −74.6 ppm in $CDCl_3$ at −60 °C. The ^1H NMR spectrum of this complex shows peaks at 1.61 and 1.43 ppm in $CDCl_3$ at −50 °C, (see Table III). At room temperature the peaks occur at 1.60 and 1.40 ppm, but instead of being in a 3:2 ratio they are now 2:1. Thus, at different temperatures different isomers predominate. The IR spectrum of this complex shows $\nu(CO_2)$ at 1693 and 1658 cm^{-1} in $CHCl_3$ solution and at 1720 and 1660 cm^{-1} in the solid state. A single $\delta(CO_2)$ band is observed at 725 cm^{-1} (Nujol mull). Very strong absorption bands corresponding to $\nu(NC)$ occur at 2234 and 2167 cm^{-1} ($CHCl_3$ solution) and at 2212 and 2132 cm^{-1} (Nujol mull) vs. 2127 cm^{-1} for pure *t*-BuNC. The other absorption bands are assignable to either *t*-BuNC or $Rh_2(O_2CCF_3)_4$. Although the solution and solid-state IR spectra are qualitatively the same, the fairly large frequency differences for a given band such as $\nu_{asy}(CO_2)$ and $\nu(NC)$ may indicate a different structure in solution. Further studies with this complex are needed to unequivocally determine its structure; it seems clear, however, that a class I adduct is not formed in contrast to $Rh_2(O_2CCH_3)_4$. It is not surprising that a 4:1 complex is formed since *t*-BuNC is a good σ donor and an excellent π acceptor. As found with pyridine, the $CF_3CO_2^-$ ligand allows *t*-BuNC to coordinate equatorially whereas the acetate does not.

Phosphorus Donors. As mentioned previously a large number of phosphine derivatives of $Mo_2(O_2CCF_3)_4$ have been reported.[6] We were interested in extending this work to $Rh_2(O_2CCF_3)_4$. The phosphorus donors used were PMe_2Ph, PPh_3, $P(OPh)_3$, and $P(OMe)_3$. Triphenylphosphine and triphenyl phosphite complexes of $Rh_2(O_2CCF_3)_4$ have been prepared and studied by X-ray crystallography.[18] We studied their solution properties. The two phosphites used here do not form adducts with $Mo_2(O_2CCF_3)_4$ presumably since they are

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Table III. ^1H and $^{31}P\{^1H\}$ NMR Data for $Rh_2(O_2CR_3)_4$ Complexes[a]

complex	nucleus	chem shift,[b] ppm	coupling const, Hz	temp, °C
$Rh_2(O_2CCF_3)_4(PPh_3)_2$	^{31}P	−32.81 d	$^1J = 166.0$	27
		−24.42 d	$J = 92.7$	
		−14.25 vw		
		−34.78 d	$^1J = 153.0$	
		−23.66 d } CCl_4 soln	$^1J = 104.5$	
		−14.8 t	$J = 37$	
$Rh(O_2CCF_3)_2(P(OMe)_3)_3$ (empirical formula)	^{31}P	+58 m	$J_{av} \cong 20$	27
		+20 m	$J_{av} \cong 20$	
		−72 t	$J = 50$	
$Rh_2(O_2CCF_3)_4P(OPh_3)_2$[c]	^{31}P	eight peaks in 161−75 ppm range, −18.2	approximately 50	27
$Rh_2(O_2CCH_2CH_2CH_3)(PPh_3)_2$	^{31}P	−18.91 br	none obsd	27
$Rh_2(O_2CCF_3)_4(t\text{-BuNC})_4$	^1H	1.61 s, 1.43 s	3:2	−50
		1.60 s, 1.40 s	2:1	27

[a] All complexes are in $CDCl_3$ solution except as otherwise noted. [b] ^{31}P chemical shifts relative to external 85% H_3PO_4; ^1H chemical shifts relative to internal Me_4Si. [c] Decomposition occurring during data collection; chemical shift of $OP(OPh)_3$ ca. −18 ppm.

not strong enough σ donors. The phosphites form axial complexes with the $Rh_2(O_2CR)_4$ system since in contrast to molybdenum there is a significant π-back-bonding stabilization. Dimethylphenylphosphine forms a class II adduct with $Mo_2(O_2CCF_3)_4$ due to its small size combined with strong basicity.[6] Thus, it would be a good candidate to form a class III adduct with $Rh_2(O_2CCF_3)_4$. Unfortunately, the reaction of $Rh_2(O_2CCF_3)_4$ with 4 equiv of PMe_2Ph yields only an intractable orange oil indicative of dimer decomposition. Triphenylphosphine lies far outside the size and basicity range described by Andersen[6] for class II adduct formation. Furthermore, in the solid state $Rh_2(O_2CCF_3)_4(PPh_3)_2$ is a typical class I adduct.[18] Thus, this complex would be unlikely to show unusual solution behavior, and one would expect a simple ^{19}F NMR spectrum such as that found with the THF adduct. This is not the case. A freshly prepared solution of $Rh_2(O_2CCF_3)_4(PPh_3)_2$ shows sharp ^{19}F NMR resonances at −74.4, −74.9, and −75.9 ppm in $CDCl_3$ at 27 °C in area ratios of 1:1:2. There is also a small peak at −75.3 ppm. At −50 °C there are still three major, sharp peaks only now in an area ratio of 1:1:1.3 (see Table I). That there is little change over this temperature range indicates that the same species are present at both temperatures, although perrhaps in differing amounts. Assignment of these peaks is difficult; presumably, they correspond to mono- and bidentate $CF_3CO_2^-$. However, the situation differs from that observed with the pyridine adduct and from the solution studies on $Mo_2(O_2CCF_3)_4$ with pyridine.[10] In those cases there are two peaks representing one class III isomer in which there is 1:1 mono- and bidentate $CF_3CO_2^-$. The more complex spectrum observed here could be a result of a mixture of isomers containing axial and equatorial PPh_3. That there would be anything other than axial coordination in solution is surprising. However, we believe that in solution the dimer may not exist. The molecular weight of $Rh_2(O_2CCF_3)_4(PPh_3)_2$ in CH_2Cl_2 was found to be 590, half the expected value of 1183. This value could result from the existence of $Rh_2(O_2CCF_3)_4(PPh_3)$ and PPh_3 in solution. However, if this were the solution structure, then only one ^{19}F NMR signal would be observed. Furthermore, a singlet corresponding to free PPh_3 would be observed in the $^{31}P\{^1H\}$ NMR spectrum or a single broad peak corresponding to fast exchange between free and coordinated PPh_3. This was not found (see Table III). Instead, three sharp signals were observed, two doublets and a weak triplet. The spectra were the same in both $CDCl_3$ and CCl_4, indicating no effect of a hydrogen-bonding solvent.

The $^{31}P\{^1H\}$ spectrum of $Rh_2(O_2CCH_3)_4(P(OMe)_3)_2$ in CD_2Cl_2 solution has been very recently reported.[28] At room temperature rapid exchange between coordinated and free trimethyl phosphite was observed leading to a single broad peak. We obtained the $^{31}P\{^1H\}$ NMR spectrum of $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$ in $CDCl_3$, and it also showed a single broad resonance at room temperature. However, these workers[28] found that at 213 K exchange was slow enough to give a useful spectrum. Signals were observed that were assigned to both $Rh_2(O_2CCH_3)_4(P(OMe)_3)$ and $Rh_2(O_2CCH_3)_4(P(OMe)_3)_2$ and free $P(OMe)_3$. The 1:1 adduct showed an AMX pattern, and the 2:1, an AA′XX′ pattern (A,A′,M = ^{103}Rh; X,X′ = ^{31}P). Presumably effective spin polarization occurs through the Rh–Rh bond (Rh 100%; $I = {}^1/_2$) that allows extensive rhodium–phosphorus and phosphorus–phosphorus coupling. By contrast, in the $Mo_2(O_2CCF_3)_4$ systems[27] no molybdenum–phosphorus (Mo 25%; $I = {}^5/_2$) or phosphorus–phosphorus coupling was observed for either class I or class II adducts. What is more relevant to this work is that by analogy with the spectrum of $Rh_2(O_2CCH_3)_4(P(OMe)_3)_2$ it is very unlikely that what exists in solution are 1:1 and 2:1 PPh_3 adducts of $Rh_2(O_2CCF_3)_4$. Nothing resembling AMX or AA′XX′ patterns is observed, and no signal for free PPh_3 is seen.

Monomeric complexes may exist in solution. A simple cleavage of the Rh–Rh bond would give $Rh(O_2CCF_3)_2(PPh_3)$. Rhodium(II) complexes are uncommon, although species such as $RhCl_2(P(Cy)_3)_2$ are known.[29] A rhodium(II) monomer does not exist in our system since the NMR spectra show no evidence of paramagnetic species (no line broadening or large isotropic shifts). Furthermore, $Rh_2(O_2CCF_3)_4(PPh_3)_2$ is EPR silent in CH_2Cl_2 solution at 77 K. The Rh(II) monomers mentioned above are EPR active as would be expected for a square-planar d^7 complex.[29] It is possible that in solution such complexes as $Rh(O_2CCF_3)_3$ and $Rh(O_2CCF_3)(PPh_3)_2$ are present in equal amounts, giving a molecular weight of 590. Another possibility is weakly associated $[Rh(O_2CCF_3)_2(PPh_3)]^-$ and the Rh(III) cation of the same formulation. A mixture of these would give the observed molecular weight as well as a variety of signals in the ^{19}F NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum favors the latter formulation, the two doublets arising from Rh(I)- and Rh(III)-coordinated PPh_3. The coupling constants are comparable to those observed for analogous rhodium complexes such as *trans*-$Rh(O_2CCF_3)(CO)(PPh_3)_2$ (J = 137 Hz)[30] and *mer*-$RhCl_3(PMePh_2)_3$ (J = 86.0 Hz).[31] The small triplet could result from a complex such as $Rh(O_2CCF_3)(PPh_3)_2$ in which there would be phosphorous–phosphorous coupling that could give peaks overlapping the rhodium coupling to give a triplet.

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The IR spectrum of $Rh_2(O_2CCF_3)_4(PPh_3)_2$ differs between solution and the solid state. In the solid a single $\nu_{asy}(CO_2)$ band is observed at 1665 cm^{-1} (Nujol mull) consistent with the bridging carboxylate structure. The other absorption bands are assignable to PPh_3 or $Rh_2(O_2CCF_3)_4$. However, in $CHCl_3$ solution $\nu_{asy}(CO_2)$ bands are observed at 1715 cm^{-1} and at 1654 and 1652 cm^{-1}. Thus, in solution some monodentate coordination occurs that would exist in $[Rh(O_2CCF_3)_2(PPh_3)]^-$, presumably a square-planar Rh(I) complex. We undertook preliminary studies of the reaction of excess PPh_3 with $Rh_2(O_2CCF_3)_4$ (see Experimental Section for details). Two main products are isolated, an orange compound that is most likely the known[25] complex $Rh(O_2CCF_3)(PPh_3)_3$ and a yellow compound best formulated as $Rh(O_2CCF_3)_3(PPh_3)_2$. The latter complex has not been previously reported although yellow $RhCl_3(PR_3)_3$ with (R = Me, Et, etc., but not phenyl)[32] is well-known. In addition, a small amount of an orange, fairly insoluble complex was obtained and is best formulated as $Rh_2(O_2CCF_3)_4(PPh_3)_4$. It is important that air be excluded from the reaction. If the reaction solution is exposed to air, triphenylphosphine oxide is produced. This was isolated as a crystalline compound, but it can also coordinate and complicate the analysis of products. Detailed investigation of these monomeric rhodium complexes is beyond the scope of this work. It appears that cleavage of the Rh–Rh bond is possible given enough phosphine, by even a bulky and relatively poor donor such as PPh_3. Furthermore, there is strong evidence that even with 2 equiv of PPh_3 monomeric Rh species are present.

With $P(OPh)_3$ results different from those for PPh_3 were obtained. Triphenyl phosphite is a poor σ donor although it has better π acceptor abilities than PPh_3. No complex of this ligand with $Mo_2(O_2CCF_3)_4$ exists, and $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$ is a typical class I adduct in the solid state.[18] Hence, it would seem very unlikely that this complex would show unusual solution behavior. This we find to be the case with one important proviso. Even under a nitrogen atmosphere in a sealed tube, a $CHCl_3$ solution of $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$ changes color over a period of days from orange-yellow to emerald green, characteristic of base-free $Rh_2(O_2CCF_3)_4$. Addition of excess $P(OPh)_3$ to a sample of this green solution leads to restoration of the original orange color. Apparently ligand oxidation to $OP(OPh)_3$ is occurring, similar to the $OPPh_3$ formation discussed earlier. A freshly prepared solution of this complex showed a single sharp ^{19}F NMR resonance at −75.1 ppm at room temperature in $CDCl_3$. However, by the time the low-temperature spectrum was obtained, decomposition had occurred, giving two main signals and several small ones in the −74.5 to −75.5 ppm region (see Table II). This rapid decomposition precluded ^{31}P NMR studies; in sealed tubes under nitrogen the green color appeared before the spectra could be completed. Nevertheless, the $^{31}P\{^1H\}$ NMR spectra that were obtained showed several signals presumably corresponding to coordinated phosphite and a sharp signal assignable to $OP(OPh)_3$ (see Table III). The solid-state IR spectrum shows a single $\nu_{asy}(CO_2)$ at 1670 cm^{-1}, and a fresh $CHCl_3$ solution shows this band at 1665 cm^{-1}. There are no differences between the two and all peaks are assignable to $P(OPh)_3$ or $Rh_2(O_2CCF_3)_4$. Kawamura and co-workers[33] have studied the frozen-solution EPR spectrum of $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2^+$ generated from the neutral dimer by γ irradiation. In addition to the expected signal, an additional signal was detected but not discussed. We suggest that this arose from $Rh_2(O_2CCF_3)_4^+$ or some other species in which the phosphite has decomposed. The mechanism for this phosphite decomposition is unknown. Presumably if the reaction proceeds stoichiometrically only trace amounts of O_2 or H_2O would be needed to effect complete oxidation with apparently little if any dimer decomposition. At any rate, $P(OPh)_3$ is too poor a σ donor and too good a π acceptor to cause other than axial coordination.

Quite different results were obtained with $P(OMe)_3$ although $Rh_2(O_2CCH_3)_4(P(OMe)_3)_2$ has been reported and is a class I adduct.[34] With this very small P donor, the Rh–Rh bond was cleaved much more readily than with PPh_3. An air-sensitive, hygroscopic yellow compound best formulated as $Rh(O_2CCF_3)_2(P(OMe)_3)_3$ by molecular weight determination and elemental analysis was isolated (see Experimental Section). However, since this complex gives a normal, diamagnetic NMR spectrum (see Tables II and III) (^{19}F and ^{31}P NMR), it is not Rh(II) but a mixture of equal amounts of monomeric Rh(I) and Rh(III) complexes. The possibility that any Rh(II) species are present can be excluded since no EPR signal was observed in CH_2Cl_2 solution at 77 K. The pale yellow color is characteristic of Rh(I) and Rh(III) phosphite complexes such as $HRh(P(OEt)_3)_3Cl_2$,[35] $HRh(P(OEt)_3)_4$,[35] $Rh_2(P(OMe)_3)_8$,[36] and $[Rh(P(OMe)_3)_5]BPh_4$.[37]

The ^{19}F NMR spectrum of the reaction product shows two sharp resonances in a 3:2 ratio at both 27 and −50 °C. The simplicity of the ^{19}F NMR spectrum is surprising since a variety of complexes could be present. One would expect a ratio of 3:1 if the complexes were $Rh(O_2CCF_3)(P(OMe)_3)_3$ and $Rh(O_2CCF_3)_3(P(OMe)_3)_3$ with only monodentate $CF_3CO_2^-$ in these square-planar Rh(I) and octahedral Rh(III) complexes.

This ratio could arise instead from different isomers. The principal species likely to be present are $[Rh(P(OMe)_3)_4]^+$ and $[Rh(O_2CCF_3)_4(P(OMe_3)_2]$, square-planar Rh(I) and octahedral Rh(III) complexes, respectively. The latter complex would have only monodentate $CF_3CO_2^-$ and could exist as both cis or trans isomers that could be present in virtually any ratio, such as 3:2, since steric constraints are not large in the two isomers. Interconversion between the two isomers would not be expected, and this accounts for the temperature independence of the ^{19}F NMR spectrum. Octahedral zerovalent or low-valent transition-metal phosphite complexes are generally stereochemically rigid.[38]

The $^{31}P\{^1H\}$ NMR spectrum of the $P(OMe)_3$ reaction product is more complex than expected for the two ions above. Multiplets are observed at +58 and +20 ppm and a smaller triplet at −72 ppm. Since the ^{19}F NMR spectrum is simple, the complexity of the $^{31}P\{^1H\}$ NMR spectrum must arise from species containing only phosphite ligands. In addition to $[Rh(P(OMe)_3)_4]^+$, other Rh(I) phosphite complexes could exist in solution. Species such as $Rh_2(P(OMe)_3)_8$[36] and $[Rh(P(OMe)_3)_5]^+$[37] are known and have complex, fluxional $^{31}P\{^1H\}$ NMR spectra that have been thoroughly analyzed. However, uncertainty about the exact products of our $P(OMe)_3$ reaction and lack of variable-temperature studies make an analysis difficult. Most likely, the observed room-temperature $^{31}P\{^1H\}$ NMR spectrum arises from a variety of Rh(I) phosphite complexes that are not stereochemically rigid combined with two isomers of a Rh(III) phosphite trifluoroacetate complex. The IR spectrum of the $P(OMe)_3$ reaction

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product confirms that only monodentate $CF_3CO_2^-$ is present. No bands are observed between 1600 and 1700 cm^{-1}, only a single broad band at 1710 cm^{-1} ($CHCl_3$ solution) or 1725 cm^{-1} (Nujol mull). Although further work is needed to characterize the reaction products, it is clear that $P(OMe)_3$ cleaves the Rh–Rh bond, causing disproportionation into monomeric Rh(I) and Rh(III) complexes. This is in contrast to $Rh_2(O_2CCH_3)_4$ in which the acetates do not allow access to the equatorial coordination sites, and dimer cleavage does not result.

It appears that reaction of $Rh_2(O_2CCF_3)_4$ with phosphorus donors results in unusual reactivity. The normally stable compounds PPh_3 and $P(OPh)_3$ are oxidized easily. The rhodium dimer itself, which remains intact when reacted with strong σ donors such as Et_3N, cannot stand up to reaction with P donors or comparable σ strength such as PMe_2Ph or $P(OMe)_3$ while a powerful σ donor with poor π acceptor abilities such as *N*-methylimidazole does not decompose the dimer as readily. The reason for this strong affinity of rhodium for P donors is not necessarily due to π-back-bonding, and it is clear that criteria such as σ basicity and ligand size are not enough to classify Lewis base reactivity of $Rh_2(O_2CCF_3)_4$.

Conclusion. The reactivity of $Rh_2(O_2CCF_3)_4$ with Lewis bases shows significant differences from the analogous $Mo_2(O_2CCF_3)_4$ and $Rh_2(O_2CCH_3)_4$ systems. The MO scheme for the two metal dimers can be used to explain the preference of rhodium vs. molybdenum for class I adducts but does not explain the high reactivity of the rhodium dimer for P donors compared to powerful σ donor and π acceptors such as pyridine and *t*-BuNC. In addition, the importance of the bridging carboxylate cannot be overemphasized. Use of fluoroacetate rather than acetate leads to products quite different from those described previously.

Experimental Section

All solvents were distilled from the appropriate drying agents before use. All bases were purified following established procedure.[35] Rhodium acetate was synthesized from $RhCl_3 \cdot 3H_2O$ by literature methods.[36] Operations were under nitrogen except as otherwise noted.

Tetrakis(trifluoroacetato)dirhodium(II). This compound was synthesized by using a modification of the procedure of Cotton and Norman for $Mo_2(O_2CCF_3)_4$.[37] Rhodium acetate (0.50 g, 1.13 mmol) was suspended in trifluoroacetic acid (10 mL) and trifluoroacetic anhydride (1 mL). The mixture was refluxed for 2 h. The solvent was then removed by pumping and the procedure repeated. The solid was recrystallized from 1:1 CH_2Cl_2:toluene to give the bright green $Rh_2(O_2CCF_3)_4$ (0.30 g, 0.91 mmol, 81%). Anal. Calcd for $Rh_2C_8F_{12}O_8$: C, 14.61; H, none; F, 34.65. Found: C, 14.65; H, none; F, 34.12. The compound decomposes in a sealed tube under nitrogen at 265 °C.

Bis(tetrahydrofuran)tetrakis(trifluoroacetato)dirhodium(II). $Rh_2(O_2CCF_3)_4$ (0.10 g, 0.15 mmol) was dissolved in THF (2.0 mL) to give a dark blue solution. Removal of solvent and recrystallization from hexane afforded blue $Rh_2(O_2CCF_3)(THF)_2$ (0.11 g, 0.14 mmol, 91%). Anal. Calcd for $Rh_2C_{16}H_{16}F_{12}O_{10}$: C, 23.92; H, 2.01; F, 28.39. Found: C, 23.61; H, 2.02; F, 28.22. The adduct loses THF at 100 °C to give $Rh_2(O_2CCF_3)_4$ and thus is a convenient form for storing $Rh_2(O_2CCF_3)_4$ since the latter compound is rather hygroscopic.

Bis(dimethyl sulfoxide)tetrakis(trifluoroacetato)dirhodium(III). This compound was synthesized following the procedure of Cotton and Felthouse.[16] $Rh_2(O_2CCF_3)_4$ (0.050 g, 0.076 mmol) was dissolved in 1:1 benzene:chloroform (5 mL). Me_2SO (0.2 mL) was added, and a blue solution resulted. The solvent was removed by pumping and the resultant solid washed twice each with toluene and hexane, leaving a blue microcrystalline solid (0.059 g, 0.07 mmol, 95%). Anal. Calcd for $Rh_2C_{12}F_{12}F_{12}S_2O_{10}$: C, 17.70; H, 1.49; F, 28.00; S, 7.88. Found: C, 19.05; H, 1.88; F, 28.32; S, 8.00.

Bis(*N*,*N*-dimethylformamide)tetrakis(trifluoroacetato)dirhodium(II). $Rh_2(O_2CCF_3)_4$ (0.030 g, 0.046 mmol) was dissolved in 1:1 methylene chloride:toluene in air. Addition of DMF (0.2 mL) led to an initial purple color, which rapidly changed to blue. Evaporation led to formation of dark blue platelike crystals (0.033 g, 0.041 mmol, 89%). Anal. Calcd for $Rh_2C_{14}H_{14}N_2F_{12}O_{10}$: C, 20.91; H, 1.76; N, 3.48; F, 28.35. Found: C, 21.30; H, 1.82; N, 3.30; F, 28.02.

Bis(triethylamine)tetrakis(trifluoroacetato)dirhodium(II). $Rh_2(O_2CCF_3)_4$ (0.50 g, 0.076 mmol) was dissolved in toluene (4 mL). Addition of Et_3N (0.1 mL) caused an immediate color change to red. Concentration to 1 mL led to formation of a red precipitate. Filtration and washing with hexane afforded a red, microcrystalline solid (0.050 g, 0.058 mmol, 76%). Anal. Calcd for $Rh_2C_{20}H_{30}N_2F_{12}O_8$: C, 27.92; H, 3.52; N, 3.26; F, 26.50. Found: C, 28.33; H, 3.56; N, 3.12; F, 25.60.

Tetrakis(pyridine)tetrakis(trifluoroacetato)dirhodium(II). $Rh_2(O_2CCF_3)_4$ (0.10 g, 0.15 mmol) was dissolved in toluene (5 mL). Addition of 2 mL of a 1:10 pyridine:toluene solution caused an immediate color change to red. Concentration to 2 mL and cooling led to formation of a red precipitate. Filtration and washing with hexane afforded a pinkish red microcrystalline solid (0.13 g, 0.13 mmol, 88%). Anal. Calcd for $Rh_2C_{28}H_{20}N_4F_{12}O_8$: C, 34.52; H, 2.07; N, 5.75; F, 23.40. Found: C, 34.98; H, 2.14; N, 5.64; F, 22.22. The compound melts in a sealed tube under nitrogen at 169–170 °C. The synthesis of $Rh_2(O_2CCF_3)_4(py)_2$ was attempted by following the procedure of Stephenson et al.[26] $Rh_2(O_2CCF_3)_4$ (0.03 g, 0.045 mmol) was dissolved in cold ethanol (2 mL). To this was added dropwise pyridine (approximately 0.2 mL). A red solution resulted, and with further cooling a red precipitate formed. Filtration and washing with hexane afforded 0.025 g. Anal. Found: C, 30.67; H, 2.05; N, 4.16. IR ($CHCl_3$ solution): $\nu_{asy}(CO_2)$ 1705 (m), 1688 (w), 1660 (s), 1650 (m) cm^{-1}. ^{19}F NMR ($CDCl_3$, 27 °C): δ −75.0 (complex m), −75.8 (5).

Tetrakis(*tert*-butyl isocyanide)tetrakis(trifluoroacetato)dirhodium(II). $Rh_2(O_2CCF_3)_4$ (0.10 g, 0.15 mmol) was dissolved in toluene (4 mL). To this solution was added *t*-BuNC (Strem Chemicals, 0.10 mL, 0.89 mmol). An orange solution immediately resulted. After 1 h, the solution was concentrated to 1 mL. Filtration and washing with hexane afforded an orange-brown solid (0.12 g, 0.12 mmol, 80%). Anal. Calcd for $Rh_2C_{28}H_{36}N_4F_{12}O_8$: C, 33.92; H, 3.66; N, 5.65; F, 23.00. Found: C, 33.67; H, 3.80; N, 5.39; F, 23.24.

Bis(acetonitrile)tetrakis(trifluoroacetato)dirhodium(II). $Rh_2(O_2CCF_3)_4$ (0.10 g, 0.15 mmol) was dissolved in air in CH_3CN (2 mL) to give a purple solution. Addition of water (3 mL) led to immediate precipitation of a purple solid. Filtration and drying in vacuo afforded 0.09 g (0.12 mmol, 80%). Anal. Calcd for $Rh_2C_{12}H_6N_2F_{12}O_8$: C, 19.45; H, 0.82; N, 3.78; F, 30.77. Found: C, 25.18; H, 1.95; N, 3.79; F, 22.65. Synthesis of this complex using only organic solvents failed to give a purer product. The complex is not air stable, CH_3CN being replaced by H_2O over a period of 1 h with a color change from purple to blue. By contrast, evaporation of an acetonitrile solution of $Rh_2(O_2CCH_3)_4$ affords a stable, purple complex that is most likely the CH_3CN adduct. Anal. Calcd for $Rh_2C_{12}H_{18}N_2O_8$: C, 27.50; H, 3.46; N, 5.34. Found: C, 27.54; H, 3.53; N, 5.02.

Bis(triphenylphosphine)tetrakis(trifluoroacetato)dirhodium(II). This compound was synthesized following the procedure of Cotton et al.[18] $Rh_2(O_2CCF_3)_4$ (0.050 g, 0.076 mmol) was dissolved in MeOH (5 mL). Triphenylphosphine (0.040 g, 0.15 mmol) was dissolved in hot MeOH (approximately 5 mL). This solution was added to the blue $Rh_2(O_2CCF_3)_4(MeOH)_2$ solution to give a dark brown color. The solution quickly became colorless, and brown needle crystals precipitated; washing with MeOH and drying in vacuo afforded 0.085 g (0.075 mmol, 94%). Anal. Calcd for $Rh_2C_{44}H_{30}P_2F_{12}O_8$: C, 44.66; H, 2.56; P. 5.23. Found: C, 43.94; H, 2.69; P, 5.18. $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$ was synthesized in the same manner and gave a satisfactory analysis.

Bis(triphenyl phosphite)tetrakis(trifluoroacetato)dirhodium(II). $Rh_2(O_2CCF_3)_4$ (0.178 g, 0.286 mmol) was dissolved in MeOH (10 mL). Triphenyl phosphite (0.150 mL, 0.572 mmol) was added dropwise to give a red-brown solution. The solution quickly became colorless, and an orange-brown microcrystalline solid precipitated. Washing with MeOH and drying in vacuo afforded 0.32 g (87.5%). Anal. Calcd for $Rh_2C_{44}H_{30}P_2F_{12}O_{14}$: C, 41.31; H, 2.35; P, 4.84. Found: C, 40.93; H, 2.25; P, 4.28.

Reaction of $Rh_2(O_2CCF_3)_4$ with Excess PPh_3. $Rh_2(O_2CCF_3)_4$ (0.162 g, 0.246 mmol) was dissolved in toluene (5 mL). Triphenylphosphine (0.640 g, 2.44 mmol) was dissolved in toluene (3 mL) and added dropwise to the green $Rh_2(O_2CCF_3)_4$ solution. A dark brown color characteristic of $Rh_2(O_2CCF_3)_4(PPh_3)_2$ resulted. The reaction mixture was stirred with heating for 1 h. During this time an orange precipitate formed. Filtration of the hot solution afforded 0.24 g. Thin-layer chromatography using 2:1 $CHCl_3$:toluene indicated two components. Extraction of the orange product with hot 1:1 toluene:CH_2Cl_2 left behind a small amount (approximately 0.05 g) of orange powder that may be a 4:1 PPh_3 adduct that precipitated before cleavage could occur. Anal. Calcd for $Rh_2C_{80}H_{60}P_4F_{12}O_8$: C, 56.29; H, 3.54. Found: C, 56.12; H, 3.87. From the toluene:CH_2Cl_2 extract an orange powder was obtained (0.15 g). This complex is most likely $Rh(O_2CCF_3)(PPh_3)_3$. Anal. Calcd for $RhC_{56}H_{45}P_3F_3O_2$: C, 67.07; H, 4.52; P, 9.27. Found: C, 67.86; H, 4.71; P, 9.58. IR (Nujol mull): single $\nu_{asy}(CO_2)$ 1678 cm^{-1} (lit.[25] 1670 cm^{-1}). Addition of hexane (5 mL) to the filtrate from the original reaction mixture and cooling led to formation of a yellow precipitate. Filtration and washing with hexane afforded 0.12 g. This compound is most likely $Rh(O_2CCF_3)_3(PPh_3)_2$. Anal. Calcd for $RhC_{42}H_{30}P_2F_9O_6$: C, 52.19; H, 3.13; P, 6.41. Found: C, 51.95; H, 3.10; P, 6.12. IR (Nujol mull): $\nu_{asy}(CO_2)$ 1710 cm^{-1}. When the above procedure is repeated without rigorous exclusion of air, the reaction proceeds in qualitatively the same manner, but $OPPh_3$ is isolated (checked by IR and elemental analysis) and the products give less satisfactory analyses due presumably to $OPPh_3$ coordination or possible side reactions.

Trimethyl Phosphite Complex. $Rh_2(O_2CCF_3)_4$ (0.169 g, 0.256 mmol) was dissolved in toluene (3 mL). To this green solution was added dropwise $P(OMe)_3$ (0.30 mL, 2.54 mmol). This reaction is fairly exothermic. A red-brown solution initially resulted, probably due to axial adduct formation. After 1 h the solution was yellow with pure yellow precipitate. Addition of hexane (2 mL) and cooling followed by filtration and washing with hexane afforded a pale yellow solid (0.30 g). Anal. Calcd for $RhC_{13}H_{27}P_3F_6O_{13}$: C, 22.27; H, 3.88; P, 13.25; mol wt 701. Found: C, 22.50; H, 3.98; P, 13.40; mol wt 698 (in CH_2Cl_2).

Experimental Methods. Elemental analyses were performed by the Microanalytical Laboratory of the University of Illinois. Fourier transform NMR spectra were recorded on a Nicolet NT-360 spectrometer operating at 338.6 MHz for fluorine and 360.1 MHz for proton. All ^{19}F chemical shifts are with respect to internal $CFCl_3$, and all ^1H chemical shifts are with respect to internal Me_4Si. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Associates XL-100 FT spectrometer operating at 40.5 MHz. The ^{31}P chemical shifts are with respect to an external standard of 85% phosphoric acid. Infrared spectra were recorded on a Nicolet 7000 FT IR for $CHCl_3$ solutions and on a Perkin-Elmer 599B instrument for Nujol mull spectra.

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Registry No. $Rh_2(O_2CCF_3)_4$, 31126-95-1; $Rh_2(O_2CCF_3)_4(THF)_2$, 90968-04-0; $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, 72665-42-0; $Rh_2(O_2CCF_3)_4(DMF)_2$, 90968-05-1; $Rh_2(O_2CCF_3)_4(Et_3N)_2$, 90968-06-2; $Rh_2(O_2CCF_3)_4(py)_4$, 90968-07-3; $Rh_2(O_2CCF_3)_4(t\text{-BuNC})_4$, 90990-41-3; $Rh_2(O_2CCF_3)_4(PPh_3)_2$, 77966-16-6; $Rh_2(O_2CCF_3)_4(P(OPh)_3)_2$, 77966-17-7; $Rh_2(O_2CCH_2CH_2CH_3)_4(PPh_3)_2$, 90968-08-4; $Rh_2(O_2CCF_3)_4(CH_3CN)_2$, 90990-42-4; $Rh(O_2CCF_3)_2(P(OMe)_3)_3$, 90968-09-5; $Rh(O_2CCF_3)(PPh_3)_3$, 34731-08-3; $Rh(O_2CCF_3)_3(PPh_3)_2$, 90968-10-8.

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Redox Properties and Demetalation of Reduced Lead Phthalocyanine in Dimethylformamide

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The electrochemical oxidation and reduction of lead phthalocyanine, PbPc, was investigated by cyclic voltammetry, rotating-disk voltammetry, and dc polarography in DMF containing 0.1 M TEAP. At a solid electrode, PbPc is electrochemically oxidized in two steps. The first oxidation is diffusion controlled and reversibly generates the monocation radical. The second oxidation also appears to be diffusion controlled by rotating-disk voltammetry but is irreversible by cyclic voltammetry under the same experimental conditions. The reduction of PbPc occurs in three reversible one-electron steps. In addition, a fourth irreversible reduction step is observed at a mercury electrode. Analysis of the current-voltage curves and characterization of the controlled-potential electrolysis products indicates that a slow demetalation occurs after the first reduction step. However, at the more rapid measurement times of cyclic voltammetry, anion radicals and dianions may be quantitatively produced. An overall oxidation-reduction mechanism is postulated, and comparisons are made between the investigated complex and the general electrochemical behavior of main-group and transition-metal phthalocyanines.

Introduction

In recent years numerous electrochemical investigations of phthalocyanines have appeared in the literature.[2-16] This recent and quite rapid development has been due, in part, to the similarity between phthalocyanines and the biologically relevant porphyrins,[17] as well as to the involvement of phthalocyanines in solar conversion systems and in electrocatalysis.

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