nitrosyl and a resonance at low field in the region of 400-500 ppm as observed for the square-pyramidal complexes of rhodium with bent apical nitrosyl ligands. Instead, the ^{15}N NMR spectrum of **12** in $(CD_3)_2CO$ shows a single resonance at 131.5 ppm at 303 K and 134.9 ppm at 183 K. The line width at half-height shows little broadening as the temperature is lowered and is 8.1 Hz at 303 K and 9.3 Hz at 183 K. The $^{31}P\{^1H\}$ NMR spectrum shows only a slightly broadened singlet in the temperature range 303-183 K (Table I). The complex does not exchange with free NO^+ at the lower temperatures but does at room temperature.

To throw further light on the structure, we measured the infrared spectra of the unenriched complex in methanolic solution. The solid gives two ^{14}NO bands in Nujol at 1860 and 1685 cm^{-1}, consistent with the presence of one linear and one bent nitrosyl ligand, as shown by X-ray crystallography. In methanolic solution, however, the nitrosyl bands show major frequency shifts and increase in number: strong absorptions are observed at 1828, 1778, and 1722 cm^{-1}, with a shoulder at 1739 cm^{-1}. After evaporation of the solvent in vacuo, the solid gave the same IR spectrum in Nujol as before, showing that no major decomposition had occurred in solution. Corresponding results were obtained with the ^{15}N-semienriched compound.

Thus, the vibrational spectra suggest the formation of two isomeric structures in solution, and it is probable that one has a trigonal-bipyramidal geometry with equivalent nitrosyl ligands similar to that reported for $[MnCl(NO)_2\{P(OMe)_2Ph\}_2]$[37] and the second a square-pyramidal structure (**12**) as in the solid[35] (possibly with coordination of the solvent). The evidence suggests that these isomers interconvert rapidly on the NMR time scale by an intramolecular process, to give a single ^{15}N resonance. Further evidence for this proposal has been obtained by studies on a 50% ^{15}N-enriched sample of $[RuCl(NO)_2(PPh_3)_2]BF_4$ for which an equlibrium isotope effect has been observed. The ^{15}N NMR spectrum of the complex is being studied in the solid state, and these results will be discussed in detail in a later paper.[38]

Acknowledgment. We thank the Science and Engineering Research Council for the provision of high-field NMR facilities, Drs. Oliver Howarth and Eirian Curzon for their help with the 400-MHz spectra run at Warwick University, and Dr. John Jeffrey of Bristol University for running the FT IR spectra.

Registry No. **6** ($PR_3 = PMePh_2$), 86501-86-2; **6** ($PR_3 = PPh_3$), 86501-87-3; **8a**, 86501-85-1; **8b**, 87306-13-6; **9**, 86501-83-9; **10a**, 86501-80-6; **10b**, 86501-81-7; **10c**, 86501-79-3; **11**, 87306-14-7; **12**, 87306-12-5; $[RhCl(SO_2)(P\text{-}i\text{-}Pr_3)_2]$, 87318-56-7.

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(38) A preliminary communication of this work has now appeared: Bell, L. K.; Mingos, D. M. P.; Tew, D. G.; Larkworthy, L. C.; Sandell, B.; Povey, D. C.; Mason, J. *J. Chem. Soc., Chem. Commun.* **1983**, 125.

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Mass Spectra of Rhenium(III) and Ruthenium(III) Complexes of 2,4-Pentanedione, 1,1,1-Trifluoro-2,4-pentanedione, and 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione

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Received December 15, 1982

The mass spectra of the title compounds have been obtained, and the results are interpreted in terms of formalisms developed from investigations of other 2,4-pentanedionato-metal complexes. The chelates of Ru(III) and Rh(III) show some unusual properties. The mass spectra of the complexes of all three ligands with ruthenium show little tendency for internal redox reactions, resulting in oxidation states for the metal other than +3. Rhodium, on the other hand, when complexed with hfa, exhibits a number of peaks that can be assigned to lower oxidation states, +2 and +1, of the metal including a peak corresponding to the $Rh(I)^+$ ion. Complexes of rhodium with tfa and acac are more similar to their ruthenium counterparts and demonstrate considerably less tendency toward reduced oxidation states. For both metals, loss of internal portions of the ligand, e.g. CO and CO_2, is observed. Apparently, migration of end groups such as methyl to the metal plays a role by forming either intermediates or transition states in these reactions. Bonds between small ligand fragments and Rh appear to be considerably more labile than comparable bonds to Ru.

Introduction

While the mass spectra of numerous complexes of transition metals with β-diketones have been published,[1] rhodium and ruthenium have been overlooked. Appearance potential data[2] and chemical ionization mass spectra[3] have been presented, but not a discussion of the ion dissociation reactions of the molecular ions. This is somewhat surprising in view of the tremendous interest in these metals as catalysts.[4] Investigations of other metal complexes have demonstrated that the mass spectrometer is a convenient apparatus to use in the examination of a number of properties of metal complexes. Gas-phase ion chemistry of these compounds has remarkable similarities with solution chemistry. Parallels have been shown with respect to redox reactions,[1] hard-soft acid-base considerations,[5] and most recently, olefin complex-forming reactions.[6] We have examined the mass spectra of the title compounds and present our findings here.

Experimental Section

Mass spectra were obtained on a Varian MAT CH-5DF reversed-geometry double-focusing mass spectrometer. An electron-impact source was operated at 70-eV ionizing voltage and maintained at 250 °C. Pressure in the source never ex-

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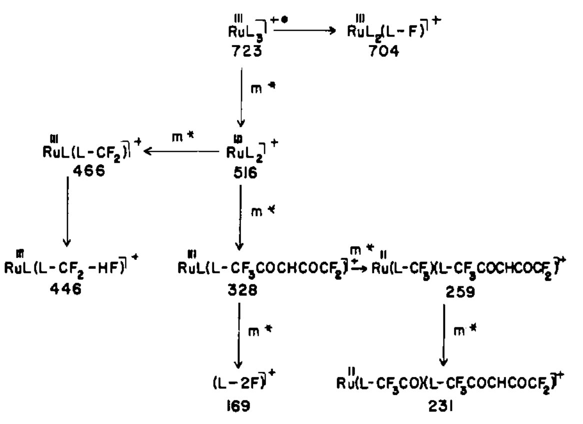
(1) For a review see: Joshi, K. C.; Pathak, V. N. *Coord. Chem. Rev.* **1977**, *22*, 37.
(2) Bursey, M. M.; Rogerson, P. F. *Inorg. Chem.* **1971**, *10*, 1313.
(3) Prescott, S. R.; Compana, J. E.; Jurs, P. C.; Risby, T. H.; Yergey, A. L. *Anal. Chem.* **1976**, *48*, 829.
(4) For example see: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980; Chapter 30.
(5) (a) Morris, M. L.; Koob, R. D. *Org. Mass Spectrom.* **1982**, *17*, 503. (b) Morris, M. L.; Koob, R. D. *Inorg. Chem.* **1981**, *20*, 2737. (c) Miller, J. M.; Jones, I. R. B.; Deacon, G. B. *Inorg. Chem. Acta* **1979**, *32*, 1979.
(6) Morris, M. L.; Koob, R. D., in preparation.

0020-1669/83/1322-3502$01.50/0 © 1983 American Chemical Society

Scheme I. Dissociation of Ru(hfa)$_3$ (L = hfa = CF$_3$COCHCOCF$_3^-$)[a]



[a] For this and all subsequent schemes, ions are represented by formulas that show apparent fragments lost from the preceding ions to give a particular peak. In the discussion, different representations may be used to imply, for example, rearrangement of the ion during the reaction. Ambiguity is avoided by expressing the associated value of *m/z* with representations as necessary.

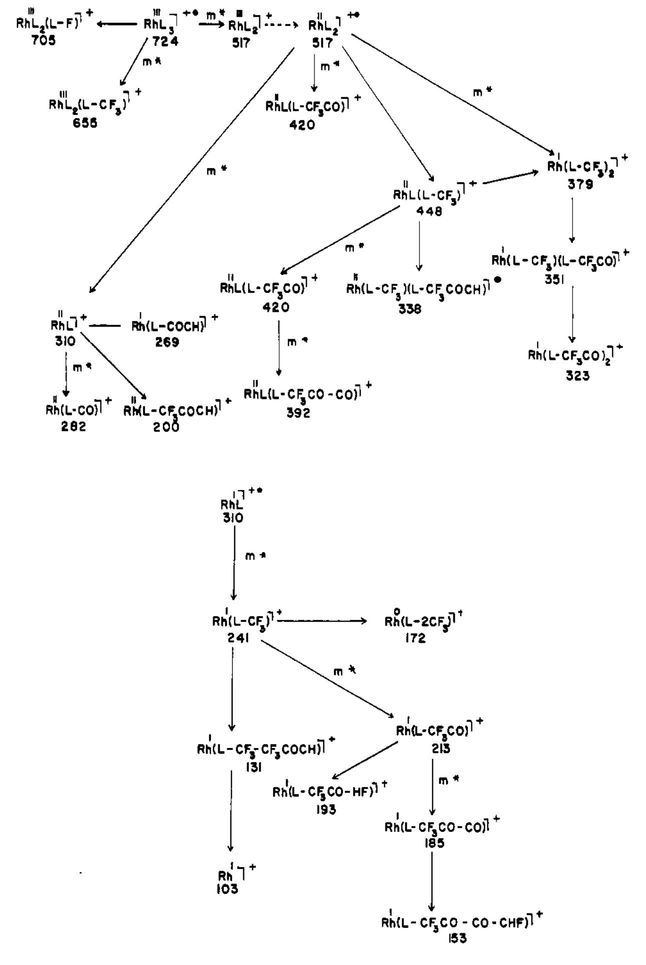
ceeded 2 × 10^{-6} torr. Samples were introduced with a solid inlet probe that was warmed from room temperature until reproducible mass scans, characteristic of the compound and with minimum background interference, were achieved. Spectra were recorded at this point. Samples were then warmed further to check for heavier impurities. None were found. Inlet temperatures did not exceed 300 °C. Metastable peak spectra were obtained by scanning the electric sector at a given setting of accelerating voltage and magnetic field.

Rh(acac)$_3$,[7] Rh(tfa)$_3$,[7] Rh(hfa)$_3$,[8] Ru(acac)$_3$,[9] and Ru(tfa)$_3$[10] were prepared by methods given in the literature. Ru(hfa)$_3$ was purchased from Strem Chemicals Inc. and was purified by vacuum sublimation at 68 °C (0.5 torr). The 2,4-pentanedione was deuterated by the method of Johnson and Everett,[9] and the Ru(III) and Rh(III) complexes of the deuterated ligand were prepared by the methods[7,9] mentioned previously. D$_2$O was used in place of H$_2$O where required.

Results and Discussion

Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)ruthenium(III), Ru(hfa)$_3$. The mass spectrum of Ru(hfa)$_3$ is among the more straightforward of the complexes examined and is readily interpreted as an analogue to Fe(hfa)$_3$. Although the Ru(hfa)$_3$ mass spectrum is somewhat less complicated than the iron spectrum, the fundamental reactions found (Scheme I) are among those seen for the iron complex.[11] Among the notable features of the spectrum is the rearrangement of a ligand-bound fluorine to ruthenium to produce one of the three most important metal-containing ions in the spectrum at *m/z* 328 (and associated isotope peaks). Processes of this type were first noted by Bancroft et al.[12] and have been observed in numerous other instances.[11,13-15] Less common is the elimination of the metal(III) trifluoride.[15] The organic ion at *m/z* 169 is related to *m/z* 328 (Ru^{III}F(hfa)$^+$) via a metastable transition that corresponds to the loss of Ru^{III}F$_3$.

Scheme II. Dissociation of Rh(hfa)$_3$ (L = hfa = CF$_3$COCHCOCF$_3^-$)



While the reaction sequence Ru(hfa)$_3^{+\cdot}$ → Ru(hfa)$_2^+$ → RuF(hfa)$^+$ accounts for more than 80% of the total metal-containing ion intensity, there are a number of minor processes that are of interest. Ru(hfa)$_2^+$ dissociates to a small degree by the loss of CF$_2$. The resulting ion appears to lose HF in a subsequent step. These reactions have been observed for both Fe^{III}(hfa)$_3$[11] and In^{III}(tfa)$_3$.[14] The first step in this sequence is presumed to be assisted by the rearrangement of a fluorine to the metal as discussed above. RuF(hfa)$^+$ (*m/z* 328) loses 69 mass units to produce an ion at *m/z* 259. If common practice is followed,[1] the resultant ion RuF(hfa − CF$_3$)$^+$ (*m/z* 259) would be assigned an oxidation state of II rather than the III of the parent compound. That this ion is of relatively low intensity reflects the stability of the higher oxidation state. This observation is more striking in contrast to the important role of metal reduction found for rhodium as discussed below. The ion at *m/z* 259 shows, via metastable transitions, even electron dissociations to peaks at *m/z* 231, 203, and 143, all of which are of low intensity. Nonetheless, the absence of other odd electron losses demonstrates that further reduction of ruthenium is not occurring.

Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(III), Rh(hfa)$_3$. The three most important peaks in the mass spectrum of Rh(hfa)$_3$ correspond to the molecular ion and the successive loss of two ligands, i.e. Rh(hfa)$_3^{+\cdot}$, Rh(hfa)$_2^+$, and

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(7) Dwyer, F. P.; Sargeson, A. M. *J. Am. Chem. Soc.* **1953**, *75*, 984.

(8) Collman, J. P.; Marshall, R. L.; Young, W.; Goalby, S. D. *Inorg. Chem.* **1972**, *1*, 704.

(9) Johnson, A.; Everett, G. W., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 1419.

(10) Everett, G. W., Jr.; Johnson, A. *J. Am. Chem. Soc.* **1972**, *94*, 6397.

(11) Clobes, A. L.; Morris, M. L.; Koob, R. D. *Org. Mass Spectrom.* **1971**, *5*, 633.

(12) Bancroft, G. M.; Reichert, C.; Westmore, J. B.; Gesser, H. D. *Inorg. Chem.* **1969**, *8*, 474.

(13) (a) Belcher, R.; Cranley, C. R.; Majer, J. R.; Stephen, W. I.; Uden, P. C. *Anal. Chim. Acta* **1972**, *60*, 109. (b) Patel, K. S.; Reinhart, K. L., Jr.; Bailar, J. C., Jr. *Org. Mass Spectrom.* **1970**, *3*, 1239. (c) Reichert, C.; Bancroft, G. M.; Westmore, J. B. *Can. J. Chem.* **1970**, *48*, 1362. (d) Das, M.; Livingstone, S. E. *Aust. J. Chem.* **1975**, *28*, 1513. (e) Livingstone, S. E.; Zimmerman, W. A. *Ibid.* **1976**, *29*, 1845. (f) Loivares, R. C.; Gomez-Lara, J.; Cortes, E. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1530.

(14) Das, M. *J. Inorg. Nucl. Chem.* **1981**, *43*, 3412.

(15) Clobes, A. L.; Morris, M. L.; Koob, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 3087.

Table I. Peaks Observed in the Mass Spectrum of $Rh(hfa)_3$

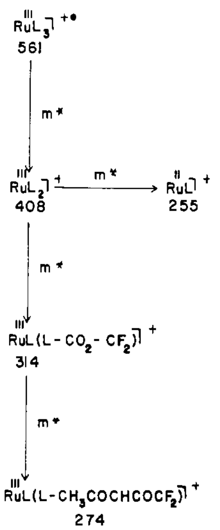
m/z	probable compn	metastable transition	% rel intens
724	$Rh(hfa)_3^{+\cdot}$		100.0
705	$Rh(hfa)_3 - F^+$		19.9
655	$Rh(hfa)_3 - CF_3^+$	724 → 655	5.9
517	$Rh(hfa)_2^+$	724 → 517	100.0
448	$Rh(hfa)_2 - CF_3^+$	517 → 448	5.2
420	$Rh(hfa)_2 - CF_3CO^+$	517 → 420	20.4
379	$Rh(hfa - CF_3)_2^+$	517 → 379	19.5
351	$379 - CO^+$		3.9
338	$379 - CHCO^+$		7.1
323	$379 - 2CO^+$		5.6
310	$Rh(hfa)^+$	517 → 310	71.4
282	$Rh(hfa) - CO^+$	310 → 282	5.4
269	$Rh(hfa) - CHCO^+$		3.0
241	$Rh(hfa) - CF_3^+$	310 → 241	27.7
213	$RhCF_3COCH^+$		21.4
200	$RhCF_3CO^+$		9.4
193	$RhC_3F_2O^+$		4.6
185	$RhC_2F_3H^+$		8.2
172	$RhCOCHCO^+$		4.7
153	$RhCF_2^+$		2.9
131	$RhCO^+$		18.7
103	Rh^+		21.7

$Rh(hfa)^+$ (Scheme II, top). These three peaks account for about 60% of the total metal-containing ion intensity. The loss of the second complete ligand is an indicator that Rh(III) has undergone reduction to Rh(II). In fact, all ions with *m/z* less than 517, $Rh(hfa)_2^+$, carry a formal oxidation number less than III. In its tendency to undergo reduction from $Rh(hfa)_2^+$, $Rh(hfa)_3$ is much like $Co(hfa)_3$.[11] Unlike the cobalt complex, however, $Rh(hfa)_3$ exhibits moderately important peaks corresponding to its further reduction to Rh(I). About 30% of the total metal-containing ion intensity is associated with ions that have a formal oxidation state of Rh(I). While many of them are small, the peaks associated with Rh(I) ions are the most numerous in the mass spectrum of $Rh(hfa)_3$. Because of the number of different peaks and the fact that $Rh(hfa)_3$ is the most unusual of the compounds discussed here, we indicate our suggestions as to the composition of the peaks corresponding to Scheme II in Table I.

Among the Rh(I) species, a number are of special interest. Perhaps the most important is the presence of a relatively important peak at *m/z* 131 corresponding to the ion $RhCO^+$. (An alternative assignment of RhC_2H_4 is discarded because there are too few hydrogens available in the ligand to allow for this composition.) This observation is important because it helps establish the usefulness of the mass spectrometer in investigating the tendency of certain oxidation states of metals to form π complexes. Another somewhat less clear-cut example of π-complex formation is the appearance of a peak at *m/z* 185, which we assign to $RhCF_2CFH^+$. The relatively strong signal obtained for Rh(I) metal ion further suggests this complex is a good candidate for bimolecular complex formation using a chemical ionization mass spectrometer and reagent gases such as CO, ethene, isobutene, etc.

Another moderately important peak is that at *m/z* 379, which we have assigned as the ion $Rh(hfa - CF_3)_2^+$. A similar species has been noted previously only with metals having a strong tendency to reduce, e.g. Cu(II) → Cu(I).[16] This ion appears to lose, in successive steps, two carbon monoxide molecules. While these are not confirmed by peaks corresponding to metastable transitions, two comparable ions, $Rh((hfa)_2 - CF_3)^+$ and $Rh(hfa - CF_3)^+$, show similar losses confirmed by metastable transitions. The latter ion is of special interest. This ion appears to exhibit an internal competition between the loss of CO and the loss of all of the remaining ligands except CO to form ions at *m/z* 213 and 131, respectively. On the basis of relative ion intensities, each process is approximately of equal probability. A similar competition is noted by $Rh((hfa)_2 - CF_3)^+$ (*m/z* 448) as well. In this case, loss of CO predominates, however.

Scheme III. Dissociation of $Ru(tfa)_3$ (L = tfa = $CF_3COCHCOCH_3^-$)



It is difficult to visualize the loss of two carbon monoxide molecules from $Rh(hfa) - CF_3)$ (*m/z* 241) without imagining a role for the metal. A fluxional transition state or reactive intermediate in which the remaining CF_3 group moves easily to the metal and back to the ligand would facilitate the release of CO. Observation of the small peak at *m/z* 172, presumably corresponding to $RhCF_3^+$, adds some support to this hypothesis. The mass spectra of $Rh(tfa)_3$ and $Rh(acac)_3$, however, provide stronger implications in this direction in that $RhCH_3^+$ is an important ion as seen below.

Tris(1,1,1-trifluoro-2,4-pentanedionato)ruthenium(III), $Ru(tfa)_3$. The base peak in the mass spectrum of $Ru(tfa)_3$ is the metal-free peak *m/z* 43, CH_3CO^+. The most intense metal-containing peak is only 29% as intense, $Ru(tfa)_2^+$. Scheme III reviews the dissociation of $Ru(tfa)_3^{+\cdot}$. It is very similar to that observed for $Ru(hfa)_3$ with two exceptions. Rather than $Ru(tfa)_2^+$ dissociating directly to RuF(tfa), it proceeds via an intermediate formed by the loss of 94 mass units. On the basis of an observation of the loss of 44 mass units for $Ru(acac)_3$ (see below), we are assigning this 94-unit mass loss to the rapid removal of CO_2 and CF_2 accompanied by rearrangement of F to ruthenium. The unsaturated hydrocarbon, allene or methyl acetylene, is then removed to yield the observed $RuF(tfa)^+$ (*m/z* 274). Also, in this region of the mass spectrum, one finds a small peak at *m/z* 270 (with accompanying isotope peaks). This peak is assigned as resulting from the migration of a methyl group to the metal to yield the ion $RuCH_3(tfa)^+$. This assignment is also given some credulity by the appearance of a relatively prominent analogue in the mass spectrum of $Ru(acac)_3$.

Examples have been given previously that compare the probability of F migration to the metal with the availability of electrons in the ligand.[5] Increasing electron availability in the ligand has generally been accompanied by the diminution of ion intensities associated with fluorine rearrangement. Such relationships have been discussed in terms of hard–soft acid–base theory (HSAB). Even though HSAB was developed on the basis of solution chemistry, it appears to have some application in rationalizing halogen rearrangement reactions.[5] The mass spectra of $Ru(hfa)_3$ and $Ru(tfa)_3$ are consistent with previous observations. The ratio $RuF(hfa)^+/Ru(hfa)_2^+$ is more than double the ratio of $RuF(tfa)^+/Ru(tfa)_2^+$. Further, the

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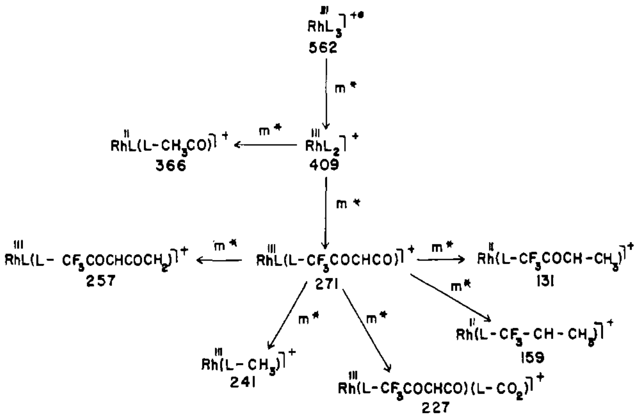
[16] Yaqub, M. M.S. Thesis, North Dakota State University, 1970.

Scheme IV. Dissociation of $Rh(tfa)_3$ (L = tfa = $CF_3COCHCOCH_3^-$)



elimination of RuF_3, which is prominent for $Ru(hfa)_3$, is absent for $Ru(tfa)_3$.

The second exception to the similarities between $Ru(hfa)_3$ and $Ru(tfa)_3$ is the point at which the apparent reduction—which is minor in both cases—occurs. For $Ru(hfa)_3$ the reduction occurs from the $RuF(hfa)^+$ ion; for $Ru(tfa)_3$ the reduction occurs from the $Ru(tfa)_2^+$ ion by the loss of a complete ligand to produce $Ru^{II}tfa^+$.

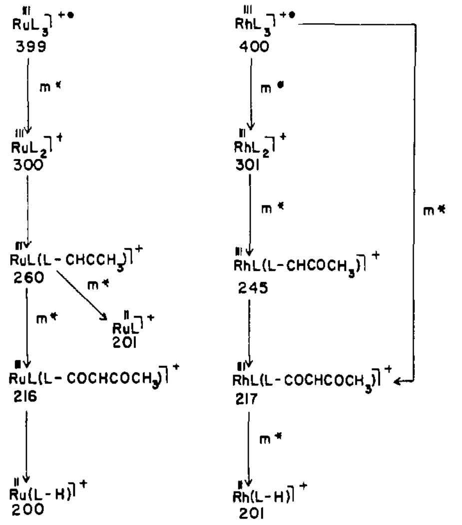
Tris(1,1,1-trifluoro-2,4-pentanedionato)rhodium(III), Rh(tfa)$_3$. Unlike the mass spectrum of $Ru(tfa)_3$, the mass spectrum of $Rh(tfa)_3$ has the metal-containing ion $Rh(tfa)_2^+$ as the base peak (*m/z* 43 with a relative intensity of 84% is still an important peak). And in sharp contrast to the case of $Rh(hfa)_3$, $Rh(tfa)_3$ exhibits no evidence whatsoever that the metal is undergoing reduction in any but the most minor of the dissociation steps. The only similarities between the mass spectra of $Rh(tfa)_3$ and $Rh(hfa)_3$ are the loss of one ligand from the molecular ion and the failure of fluorine to migrate to the metal. Fluorine migration to metal is so common in fluorinated ligands of this type[11-16] that the failure to observe it in compounds such as those of Cu(II) has been rationalized to result from competition from the very fast internal reduction reaction.[17] The failure to observe fluorine migration in $Rh(hfa)_3$ when it is so important for $Ru(hfa)_3$ could have been rationalized in the same manner. For $Rh(tfa)_3$, however, internal reduction of the metal is not at all important. Yet migration of fluorine to the metal is not observed. What is observed as the third most important metal-containing ion, after the molecular ion and the base peak, is a peak corresponding to a methyl migration to the metal, $RuCH_3(tfa)^+$ (Scheme IV), at *m/z* 271. This ion decomposes via a number of metastable transitions to at least five more minor ions (*m/z* 257, 241, 227, 159, and 131). The last two peaks correspond to $Rh(CO)_2^+$ and $Rh(CO)^+$, respectively. A peak at *m/z* 103 corresponding to Rh^+ is also observed but is relatively less important than in $Rh(hfa)_3$.

To our knowledge, Rh is the only example of the metals so far investigated that shows such sensitivity to changes in ligand composition. $Rh(tfa)_3$ is much more similar to $Rh(acac)_3$ than to $Rh(hfa)_3$ with respect to its dissociative behavior. One can only postulate that in the kinetically controlled display that is a mass spectrum, the presence of the hydrocarbon portion of the molecule introduces reactions that occur rapidly enough to exclude an important role for the reduction step.

Table II. Peaks with a Relative Intensity of More Than 5% of the Base Peak in the Mass Spectrum of $Rh(acac)_3$

m/z	probable compn	metastable transition	% rel intens
400	$Rh(acac)_3^{+\cdot}$		62.73
301	$Rh(acac)_2^+$	400 → 301	100.00
245	$Rh(acac)(CO)(CH_3)^+$	301 → 245	6.88
231	$Rh(acac)(CO)H^+$		8.21
217	$Rh(acac)(CH_3)^+$	400 → 217	30.22
203	$Rh(acac)H^+$		22.00
201	$Rh(acac - H)^+$	217 → 201	17.78
187	$Rh(acac - CH_3)^+$		5.80
173	$RhC_4H_6O^+$		14.41
172	$RhC_4H_5O^+$		6.16
159	$Rh(CO)_2^+$, $RhC_2H_4CO^+$		6.86
157	$RhC_2H_2CO^+$		11.16
146	$RhCH_3CO^+$		6.60
145	$RhCH_2CO^+$		6.77
144	$RhCHCO^+$		8.81
143	$RhC_3H_4^+$		6.66
131	$RhCO^+$, $RhC_2H_4^+$		11.38
130	$RhC_2H_3^+$		5.16
129	$RhC_2H_2^+$		6.24
103	Rh^+		6.33
43	CH_3CO^+		36.05

Scheme V. Dissociation of $Ru(acac)_3$ and $Rh(acac)_3$ (L = acac = $CH_3COCHCOCH_3^-$)



Tris(2,4-pentanedionato)rhodium(III), Rh(acac)$_3$. Table II lists the peaks in the mass spectrum of $Rh(acac)_3$ (Scheme V) that have a relative intensity of greater than 5% of the base peak. As with $Rh(tfa)_3$, the base peak is the bis complex ion $Rh(acac)_2^+$ and the molecular ion and *m/z* 43 are the other two most important ions in the spectrum. Also in close analogy with the mass spectrum of $Rh(tfa)_3$, one finds peaks corresponding to $Rh(acac)CH_3^+$, $Rh(acac)H^+$, $Rh(CO)_2^+$, $Rh(CO)^+$, and Rh^+. Deuteration of $Rh(acac)_3$ provides a distinction between contributions to *m/z* 131 from $RhCO^+$ and $RhC_2H_4^+$. The alkene complex does make some contribution to this peak as well as to *m/z* 159, although there appears to be no doubt that $RhCO^+$ and $Rh(CO)_2^+$ are present as would be inferred by comparison to the mass spectrum of $Rh(tfa)_3$. Alkene or alkyne complexes also appear to provide the best rationalization of peaks found at *m/z* 129, 130, and 143. Comparable peaks are much less important (at least a factor or two) in the $Rh(tfa)_3$ spectrum. Combinations of acetylene with CO and CO + CH_3 may be used to rationalize *m/z* 157 and 172, respectively. Analogues to *m/z* 245 and 231 are also of very low intensity in the $Rh(tfa)_3$ spectrum. The metastable transition (217 → 201) coresponds to the loss of methane and suggests the possibility of the metal center serving as the site of the elimination. A comparable reaction appears to be the source of the peak at *m/z* 187 (203 → 187) since the more usual explanation for the appearance of such a peak, methyl loss from $Met(acac)^+$, is weakened by the absence of significant intensity due to $Rh(acac)^+$. The apparent ease with

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[17] Morris, M. L.; Koob, R. D. *Org. Mass Spectrom.* **1983**, *18*, 305.

which Rh(acac)$_3$-derived ions can form metal–carbon and metal–hydrogen bonds is certainly consistent with the well-known catalytic activity of reduced-valence rhodium compounds.

One minor process is worth noting because of its relationship to the mass spectrum of Ru(acac)$_3$ discussed below. Rh(acac)$_2^+$ loses 40 mass units to produce an ion with m/z 261 by loss of a purely hydrocarbon fragment (C_3H_4). The composition of this oxygen-free fragment is confirmed by the deuteration experiment. The resulting ion then loses CO_2 to become Rh(acac)CH$_3$ (m/z 217).

Tris(2,4-pentanedionato)ruthenium(III), Ru(acac)$_3$. The predominant ions in the mass spectrum of Ru(acac)$_3$ include the molecular ion, Ru(acac)$_3^{+\cdot}$, Ru(acac)$_2^+$, and CH_3CO^+. The remaining more intense ions (relative intensity greater than 15% of the base peak) are accounted for by the reaction sequence mentioned in the previous paragraph for Rh(acac)$_3$. Instead of a minor process, however, the sequence of the loss of C_3H_4 from Ru(acac)$_2^+$ to yield Ru(acac)(CH$_3$)(CO$_2$)$^+$ (m/z 260) followed by the loss of CO_2 to yield Ru(acac)CH$_3^+$ (m/z 216) is a relatively important reaction sequence entirely supported by the observation of peaks corresponding to metastable transitions (Scheme V). The assigned compositions are further supported by the mass spectrum of the partially deuterated Ru(acac)$_3$.

The remainder of the mass spectrum of Ru(acac)$_3$ is characterized by a number of less intense multiplets in the mass range of 120–200. These multiplets appear to correspond to the hydrocarbon-containing fragments noted in Table II for Rh(acac)$_3$. Because of their relatively low intensities, we have not attempted to assign compositions. The task is considerably complicated by the multiisotope nature of Ru and the one or two hydrogen atom difference separating some of these ions.

Summary

Both rhodium and ruthenium appear to play an important role in facilitating internal rearrangement in the complexing ligands. Such rearrangements seem likely to occur via the formation of bonds between the metal center and portions of the ligand, e.g. F., CO, CH$_3$, and H. The main difference between the two metals is the stability of the metal–(small fragment) bond. Ruthenium binds irreversibly (in the context of the mass spectrometric experiment) to F and CH$_3$, and the free metal ion is not osberved. Bonds to rhodium, on the other hand, appear more easily made and broken, and numerous metal-containing species develop as well as the free Rh(I) ion. The ease of making and breaking bonds to rhodium would seem to be an important aspect of its well-known catalytic activity.

Acknowledgment. The authors thank Mark A. Carlson for obtaining the mass spectra discussed above.

Registry No. Rh(acac)$_3$, 14284-92-5; Rh(tfa)$_3$, 14652-54-1; Rh(hfa)$_3$, 14038-71-2; Ru(acac)$_3$, 14284-93-6; Ru(tfa)$_3$, 16702-38-8; Ru(hfa)$_3$, 16827-63-7.

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Mössbauer Study of Imidazole and N-Heterocyclic Complexes of Pentacyanoiron(II) and Pentacyanoiron(III)

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Received March 8, 1983

The Mössbauer spectra of (CN)$_5$Fe^{II}L^{3-} and (CN)$_5$Fe^{III}L^{2-} salts have been obtained for L = a series of imidazoles, pyrazoles, pyridines, and pyrazines. The Fe(II) complexes of the imidazoles behave normally with center shifts close to 0.29 mm/s and quadrupole splittings, Δ, equal to 0.65 mm/s (1-methylimidazole) to 0.87 mm/s (*l*-histidine). A plot of the $^1E_{(1)} \leftarrow {}^1A_1$, d–d transition energy vs. the center shift is linear, both quantities related to $\sigma + \pi$ effects on the bonding. The imidazoles are shown to fall on a line established by "σ-only" ligand donors, while pyridines and pyrazines fall off the line of positive slope and to the right when center shift ($\sigma + \pi$ parameter) is plotted vs. quadrupole splitting, a $\sigma - \pi$ parameter. Thus, imidazoles are shown to be very weak π acceptors compared to the more aromatic heterocyclic ligands, whose complexes also exhibit well-defined metal-to-ligand charge-transfer (MLCT) bands. The Fe(III) complexes are studied in detail here for the first time. Golding's predicted upper limit to Δ of 2.54 mm/s for (CN)$_5$FeL^{2-} ions with large distortions from octahedral symmetry has been experimentally demonstrated. Ligands are found to influence Δ for (CN)$_5$FeL^{2-} complexes as two distinct sets of ligands. For heterocyclic rings containing an additional nonbonding lone pair either internal or exo (and resonant) with the ring, Δ approaches Golding's limit. The value of Δ is almost independent of the σ strength of L over 7 pK_a units. The same set of complexes possess a ligand-to-metal charge-transfer (LMCT) band in the visible electronic region. Ligands meeting these criteria include the imidazoles, benzimidazole, pyrazoles, and aminopyridines. This group must be better π donors than CN$^-$. By contrast, heterocyclic rings with no internal or exo nonbonding lone pairs produce (CN)$_5$FeL^{2-} complexes with no LMCT band and have Δ values approximately proportional to the σ donor strength of L as estimated by protonic pK_a's. The center shifts of the Fe(III) complexes vary between 0.11 and 0.20 mm/s; the differences are mostly due to variation in the cation from Ca^{2+}, Zn^{2+}, Na$^+$, and *N,N'*-dimethyl-1,4-diazoniabicyclo[2.2.2]octane ion.

Introduction

A number of physical, thermodynamic, and kinetic properties of imidazole and imidazolate complexes of pentacyanoiron(II) and -iron(III) have been reported by our laboratory[1,2] and by others.[3-5] For the Fe(III) complexes, (CN)$_5$FeL^{2-}, a ligand-to-metal charge-transfer (LMCT) band is observed with N-heterocyclic ligands, L, that have lone pairs in addition to the bonding lone pair at N. We have examined the low-spin Fe(II) and Fe(III) complexes of a series of N-heterocyclic complexes with the goal of evaluating aspects of the bonding to N-heterocyclic ligands, in particular the imidazole family, by means of Mössbauer-effect spectroscopy. A significant amount of literature exists for the Mössbauer

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(1) Johnson, C. R.; Shepherd, R. E.; Marr, B.; O'Donnell, S.; Dressick, W. *J. Am. Chem. Soc.* **1980**, *102*, 6227–6235.

(2) (a) Shepherd, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 3329–3335. (b) Bowers, M. L.; Kovacs, D.; Shepherd, R. E. *Ibid.* **1977**, *99*, 6555–6561.

(3) Toma, H. E.; Batista, A. A.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 7509–7515.

(4) Toma, H. E.; Martins, J. M.; Giesbrecht, E. *J. Chem. Soc., Dalton Trans.* **1978**, 1610–1617.

(5) Szecsy, A. P.; Haim, A. *J. Am. Chem. Soc.* **1981**, *103*, 1679–1683.