Reactions of Pd, Ni, and Cu Metals with Trifluoroacetic Anhydride

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The reactions of trifluoroacetic anhydride with palladium, nickel, and copper atoms at low temperatures have been studied by spectroscopic and synthetic techniques. Results indicate that metal–anhydride complexes are formed at low temperatures and subsequently decompose to give metal trifluoroacetates upon warming to ambient. The order of stability of these complexes is believed to be Ni < Cu < Pd. The reaction of Ni(CO)₄ with trifluoroacetic anhydride also yields bis(trifluoroacetate) nickel.

Introduction

Klabunde and co-workers have shown that the co-condensation of palladium atoms with trifluoroacetic anhydride (TFAA) at 77 K produced a brown solid which dissolved in ether and continually deposited palladium metal upon standing at room temperature over a one-hour period [1]. The nature of the palladium–anhydride interaction was not determined although results of trapping experiments yielding $Pd(O_2CCF_3)_2(PEt_3)_2$ were interpreted to mean that formation of a Pd(0) anhydride complex was likely. Our interest in this work has been in the synthesis and subsequent decomposition of pseudo-stable complexes to yield metal films. Consequently, we have undertaken a study of not only the palladium reaction, but also the reactions of nickel and copper atoms with TFAA in order to determine the nature of the metal–anhydride complex.

Experimental

General

Metal atom reactions on a synthetic scale were carried out using an apparatus similar to that described by others [2]. The reactor was chemically dried with a separate portion of TFAA and evacuated overnight prior to each experiment. Vacuum system manipulations were carried out in a Pyrex system equipped with greaseless Kontes glass/Teflon valves. Routine infrared spectra were recorded on a Perkin-Elmer 467 spectrometer using a 10-cm glass cell equipped with KBr windows. NMR spectra were obtained using a Varian EM-390 spectrometer operating at 84.68 MHz for fluorine nuclei, and mass spectra were recorded using a CVC MA2 time-of-flight spectrometer operating at 70 eV. Solvents were degassed and dried as follows: acetone, $CaSO_4$; diethyl ether, $LiAlH_4$; methylene chloride and
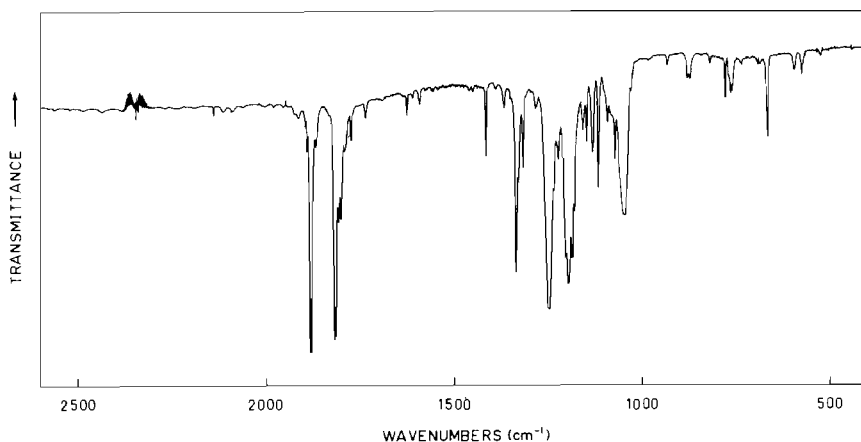

Fig. 1. Infrared Spectrum of TFAA in Ar Matrix at 12 K (Ar/TFAA = 200/1).

TABLE I. Infrared Spectroscopic Data for TFAA in Ar Matrix in the 2000–400 cm^{-1} Region (Ar/TFAA = 200/1).

1915 vw	1365 w	1115 m
1895 vw	1335 s	1090 w
1892 w	1328 m,sh	1073 m
1883 vs	1315 m	1045 s
1862 w,sh	1280 w	930 vw
1818 vs	1247 s	878 w
1815 vs	1233 m,sh	870 w
1807 m,sh	1223 w	818 vw
1802 m,sh	1208 m,sh	777 w
1790 w,sh	1203 s,sh	763 w
1775 w	1195 s	758 w
1735 w	1185 s,sh	733 w
1625 w (H_2O)	1180 m,sh	665 m
1590 vw (H_2O)	1158 w	595 vw
1415 m	1148 m	575 vw
1390 vw	1130 m	523 vw

toluene, P_2O_5. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The matrix isolation technique used in the present work has been described in detail before [3]. Briefly, matrix samples were prepared by co-condensing argon-diluted TFAA (200:1) with thermally evaporated metal atoms onto a CsI window at 10 K. The gas samples were deposited at a rate of 0.5 mmol per hour for 6 to 7 hours. Matrix spectra were obtained using a Digilab FTS-15C interferometer in the 4000–400 cm^{-1} spectral region by accumulating 100 scans at 0.5 cm^{-1} resolution. For spectra shown

here, only relative intensities of bands within the same spectrum are meaningful.

Background spectra were obtained similarly by scanning the substrate window during the cool-down period prior to sample deposition. Spectra were also obtained after final sample deposition at temperatures between 70 and 298 K. These experiments were performed by carefully warming the matrices to remove the argon and spectroscopically examining the residue on the window *in vacuo* to determine any temperature-dependent change. The cryostatic cold station was held at the desired temperature by a resistive heater or by turning off the refrigerator periodically. Window temperatures were measured with a gold–0.07% iron *vs.* chromel thermocouple imbedded in the window mount.

Matrix Isolation Experiments

The infrared spectrum of a 200/1 Ar/TFAA matrix at 12 K in the region from 2600–400 cm^{-1} is shown in Fig. 1. As the data in Table I show, the principal carbonyl stretching vibrations were found at 1883, 1818, and 1815 cm^{-1}. Upon co-condensing thermally evaporated palladium, copper, and nickel atoms with the Ar/TFAA mixture in separate experiments, new bands were observed in the 1700–1400 and 1000–700 cm^{-1} frequency ranges as shown in Figs. 2a, 3a, 4a, and Table II. The closely-spaced sharp peaks in the 1550–1300 cm^{-1} area were due to water vapor that was not completely subtracted from the sample spectrum.
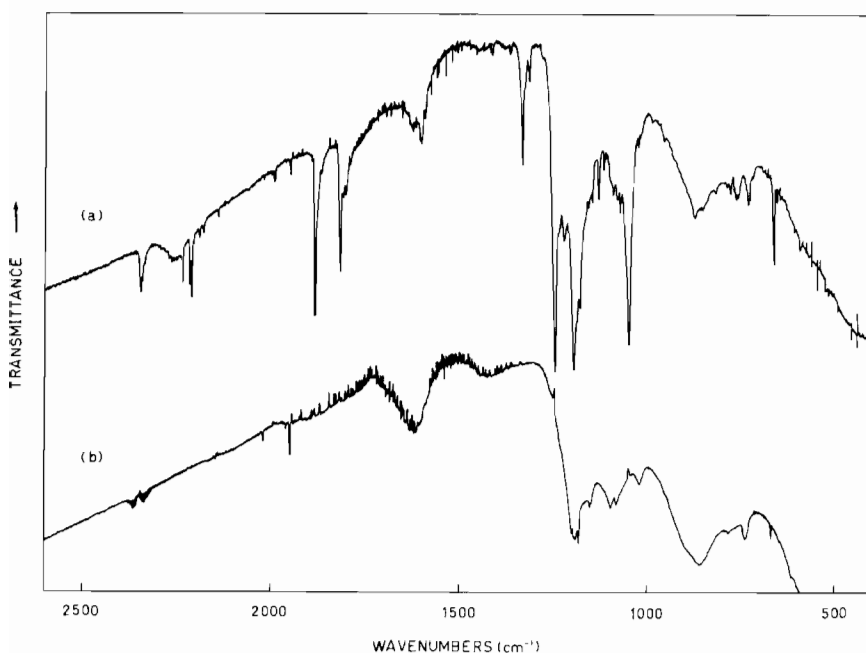

Fig. 2. a) Infrared Spectrum of Pd + TFAA in Ar Matrix at 12 K. b) Infrared Spectrum of Residue on Window at −20 °C from Pd + TFAA Reaction.

TABLE ll. New Absorptions in the 2000–400 cm^{-1} Region of the Infrared Spectra of Metal Atom–TFAA Co-Condensation Reactions in Ar Matrices at 12 K.

Pd	Cu	Ni
		1738
1625	1635	1640
		1618
1605	1590	1590
	1585	1585
	1580	1577
1450	1465	
1380		
985		985
		980
955		950
855	855	865–860
	790	790
		745
730	732	735

Metal-Atom Reactor Experiments

Pd + TFAA

Palladium metal (246 mg, 2.32 mmol) was evaporated from an alumina crucible by resistive heating and condensed with TFAA (5.512 g, 26.25 mmol) at −196 °C over a two-hour period to give a dark brown matrix. In order to remove unreacted TFAA and any very volatile side-products, the liquid nitrogen around the reactor was replaced with a −45 °C slush bath, and the reactor opened to a vacuum trap at −196 °C. A trace amount of non-condensable gas was detected during the early stages of transfer. When the transfer at −45 °C was complete, additional volatile materials were collected in a separate trap by allowing the reactor to warm to ambient temperature; the intent here was to determine if a complex of low to intermediate stability were decomposing. Further separate collections were made overnight and then again after the reactor remained at ambient conditions for two days. The
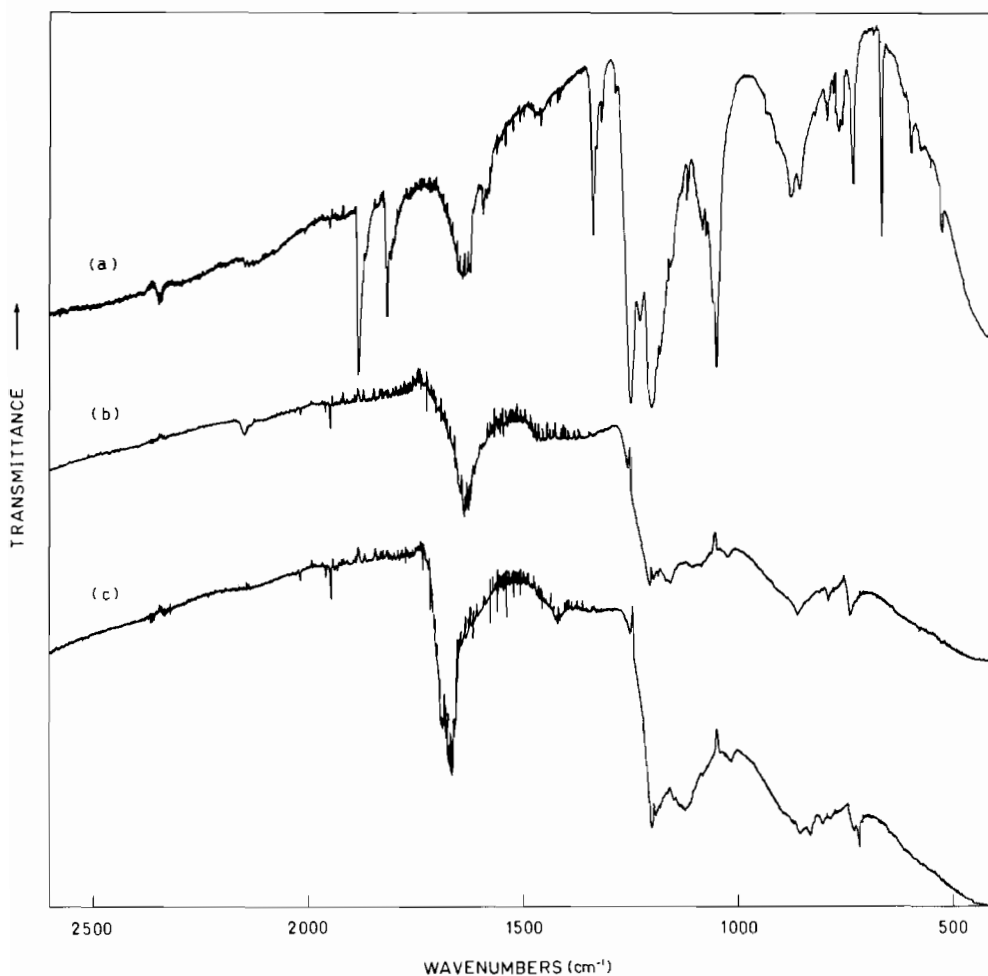

Fig. 3. a) Infrared Spectrum of Cu + TFAA in Ar Matrix at 12 K. b) Infrared Spectrum of Residue on Window at −15 °C from Cu + TFAA Reaction. c) Infrared Spectrum of Residue on Window at Room Temperature from Cu + TFAA Reaction.
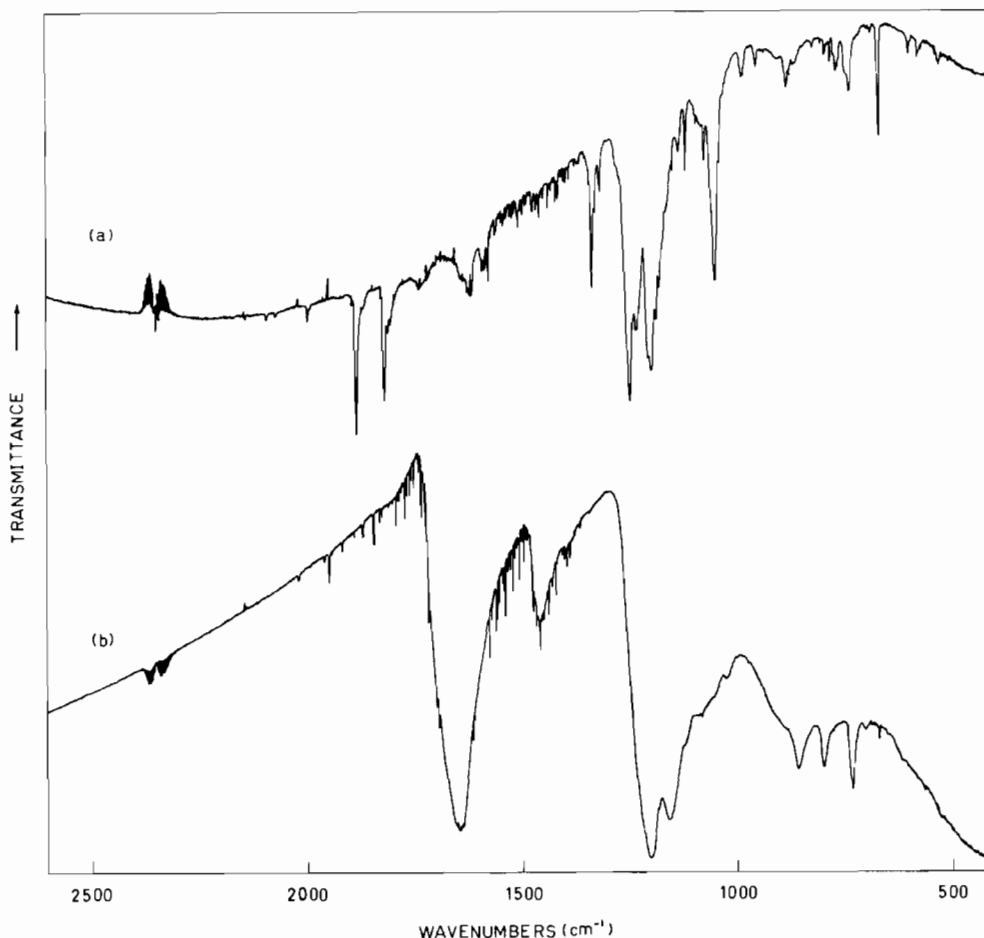
Fig. 4. a) Infrared Spectrum of Ni + TFAA in Ar Matrix at 12 K. b) Infrared Spectrum of Residue on Window at Room Temperature from Ni + TFAA Reaction.

materials collected were separated by fractional condensation through a series of traps at −63, −96 and −196 °C. The volatile material collected from the reactor at −45 °C yielded TFAA (5.156 g, 24.55 mmol) and CF_3COF (0.09 mmol), whereas that collected between −45 °C and ambient yielded TFAA (0.38 mmol) and a trace of CF_3COOH. Separation of the volatile materials collected at ambient conditions produced 0.28 mmol of TFAA overnight and an additional 0.41 mmol after standing for two days.

In a separate experiment carried out to examine the non-volatile products, approximately 10 ml of dry ether were condensed into the reactor after removing the material volatile at −45 °C. The reactor and contents were then warmed to room temperature and the solution withdrawn and filtered under a nitrogen atmosphere to give a dark brown filtrate. The solution slowly deposited a black solid (presumably palladium black) upon standing at room temperature. An infrared spectrum of a film deposited on a KBr disk after evaporation of the ether

under nitrogen contained the following bands: 1880(w), 1700(sh), 1670(m), 1200(s), 1160(s), 885(m), 840(w), 790(w), 725(m), 705(w). Exposure of the film to air resulted in the formation of a narrower, more intense band at 1685 cm^{-1} as well as a broad OH band at 3530 cm^{-1} and more subtle changes in the CF_3 region of the spectrum.

Cu + TFAA

Copper metal (281 mg, 4.41 mmol) was evaporated from an alumina crucible and condensed with TFAA (7.335 g, 34.93 mmol) during a three-hour period to give a dark purple matrix. The warming procedure was the same as that used in the palladium experiment except that no attempt was made to collect volatile material from the reactor beyond an overnight period at ambient conditions since no additional material was seen to be transferring. The volatile materials collected at the various temperatures were found to contain the following compounds: at −45 °C, CF_3COF (0.08 mmol) with a trace of $CF_3C(O)C(O)CF_3$ and TFAA (31.39

mmol); −45 °C to ambient, CF$_3$COF (0.03 mmol), TFAA (0.62 mmol), and CF$_3$CH(O$_2$CCF$_3$)C(O)CF$_3$ (0.27 mmol). The latter was identified by molecular weight (calcd, 292.1, found by vapor density measurements, 290.9); infrared (2960 cm^{-1} (vvw), 1820(m), 1792(w), 1330(w), 1275(m), 1245(m), 1200(s), 1160(m), 1140(m), 990(w), 925(w), 735(m)); NMR (^{1}H, quartet, δ = −6.03 ppm, J = 6.0 Hz); ^{19}F, doublet of overlapping quartets, δ = +72.8 ppm (relative to F-11), J$_{FF}$ = 3.9 Hz, J$_{HF}$ = 6.1 Hz; singlet, δ = +75.7 ppm; quartet, δ = +77.3 ppm, J$_{FF}$ = 3.9 Hz); and mass spectroscopy (273 (P − 19), C$_6$F$_8$O$_3$H$^+$; 245, C$_3$F$_8$O$_2$H$^+$; 223, C$_3$F$_6$O$_3$H$^+$; 195, C$_3$F$_5$O$_4^+$; 179, C$_3$F$_5$O$_3^+$; 167, C$_2$F$_5$O$_3^+$; 129, C$_3$F$_4$OH$^+$; 97, C$_2$F$_3$O$^+$; 79, C$_2$F$_2$OH$^+$; 78, C$_2$F$_2$O$^+$; 69, CF$_3^+$; 51, CF$_2$H$^+$; 50, CF$_2^+$). The volatile materials that were collected overnight were identified as CF$_3$COF (0.05 mmol) and TFAA (0.67 mmol).

After removal of the volatile materials, approximately 20 ml of dry toluene were condensed into the reactor in order to dissolve the nonvolatile reaction products, and the mixture warmed to ambient with stirring. The suspension was withdrawn from the reactor and filtered to give a clear brown filtrate. Removal of the toluene left 362 mg of a gray solid which melted with decomposition at 198–200 °C. An elemental analysis of a portion of this material found C, 13.51%, H, 0.42%, F, 29.89% and Cu, 33.60% (calculated for CuO$_2$CCF$_3$; C, 13.61%; H, 0%; F, 32.28%; Cu, 35.99%). The infrared spectrum of a paraffin-oil mull contained bands at 1630(s), 1235(sh), 1220(vs), 1165(s), 1145(s), 855(m), 780(s), 730(w), 550(w), 515(m), 490(w). The residue left on a KBr disk after evaporating several drops of a methylene chloride solution also contained a medium intensity band at 1465 cm^{-1} in addition to those already listed. The NMR spectrum of a CH$_2$Cl$_2$ solution with F-11 as an internal standard contained a broad band ($\nu_{1/2}$ = 9.9 Hz) 74.5 ppm upfield from F-11.

Ni + TFAA

Nickel metal (325 mg, 5.54 mmol) was evaporated from an alumina crucible and condensed with TFAA (6.592 g, 31.39 mmol) at −196 °C during a two-hour period to give a red-brown matrix. The warm-up procedure was the same as that followed in the copper experiment. The volatile materials collected at the various temperatures were found to contain the following components: at −45 °C, CF$_3$COF (0.33 mmol) with a trace of Ni(CO)$_4$, and TFAA (26.25 mmol); at −45 °C to ambient, CF$_3$COF (0.09 mmol) and TFAA (0.20 mmol); ambient conditions overnight, CF$_3$COF (0.13 mmol) and trace quantities of CF$_3$COOH. The reactor was opened to the atmosphere, the walls washed with acetone, and the washings collected and filtered to give a green solu-

tion. Evaporation of the solvent gave a light green powder, which, upon drying at 120 °C *in vacuo* overnight, turned light brown (weight = 830.5 mg). The infrared spectrum of a paraffin-oil mull of this material contained the following bands:

1650(s−br), 1210(sh), 1195(s−br), 1160(s), 1020(w), 855(m), 790(m), 725(m), 610(w), 520(m). This is in reasonable agreement with that reported for Ni(O$_2$CCF$_3$)$_2$ by Sharp *et al.* [4] and the material identified as Ni(O$_2$CCF$_3$)$_2$ from the Ni(CO)$_4$–TFAA reaction.

The behavior of non-volatile products was examined in a separate experiment by condensing approximately 20 ml of dry ether and one ml of dry acetone into the reactor after removing all of the volatile material. The suspension was then removed and filtered under nitrogen to give a clear, dark brown filtrate which did not change in appearance after standing for two weeks at ambient conditions. Evaporation of the solvent from several drops of this solution on a KBr disk gave a film whose infrared spectrum contained the following absorptions: 3540(m−br), 1720(s), 1680(s), 1460(m), 1365(m), 1200(s), 1150(s), 1090(w), 850(m), 795(m), 730(m), 515(w).

Ni(CO)$_4$ + TFAA

Nickel tetracarbonyl (3.67 mmol) and TFAA (2.83 mmol) were condensed into a 60 ml Pyrex vessel at −196 °C and allowed to remain at ambient conditions for three weeks. During this time, the mixture was periodically frozen to −196 °C and the non-condensable gas removed. A red-brown solid slowly formed and gradually turned dark brown. Removal of the volatile materials from the reaction flask and distillation into a −96 °C trap yielded a mixture of Ni(CO)$_4$ + CF$_3$COF (0.52 mmol), a mixture of Ni(CO)$_4$ + TFAA (2.49 mmol), and a trace of yellow liquid believed to be CF$_3$C(O$_2$CCF$_3$)-(C(O)CF$_3$)$_2$: gas-phase infrared spectrum (1845(s), 1690(w), 1330(m), 1310(m), 1240(vs), 1210(vs), 1190(vs), 1175(m), 1145(m), 1100(vs), 1065(vs), 940(m), 895(w), 875(w), 845(w), 770(w), 750(m), 710(w), 670(w)), mass spectrum (388, C$_8$F$_{12}$O$_4^+$; 369, C$_8$F$_{11}$O$_4^+$; 341, C$_7$F$_{11}$O$_3^+$; 291, C$_6$F$_9$O$_3^+$; 275, C$_6$F$_9$O$_2^+$; 225, C$_5$F$_7$O$_2^+$; 175, C$_4$F$_5$O$_2^+$; 97, C$_2$F$_3$O$^+$; 78, C$_2$F$_2$O$^+$; 69, CF$_3^+$; 50, CF$_2^+$). The infrared spectrum of a paraffin-oil mull of the light brown solid residue contained the following bands: 1655(s), 1200(s), 1165(s), 835(w), 800(w), 790(w), 725(m), 715(m), 510(w) and was in reasonable agreement with the spectra of the material obtained from the nickel atom–TFAA reaction and that reported for Ni(O$_2$CCF$_3$)$_2$ [4]. The solid did not melt at temperatures up to 360 °C; heating with a gas flame to approximately 700 °C *in vacuo* produced a mixture of volatile materials containing CO$_2$, CF$_3$COF and SiF$_4$ (the latter forming presumably through the reac-

TABLE III. Summary of Infrared Spectroscopic Data in the 2000–400 cm^{-1} Region from Warm-up Experiments of Metal Atom–TFAA Matrix Isolation Reactions.

Pd (−20 °C)	Cu (−15 °C)	Cu (R.T.)	Ni (R.T.)
		1690	
1625	1635	1667	1655
1425		1425	1460
1200	1205	1200	
1192	1195	1190	1195
1182	1185		
1150	1160		1150
		1125	
1095			
1080			
855	860	855	860
		830	
		803	
780	790		795
735	740	730	735
		720	

tion of F$^-$ with SiO$_2$ in glass). Elemental analysis of the solid gave the following results: C, 17.37%; H, 0.4%; F, 38.25%; Ni, 21.42% (calculated for Ni(O$_2$CCF$_3$)$_2$: C, 16.86%; H, 0%; F, 40.04% Ni, 20.62%).

Results and Discussion

The combined results of matrix isolation and metal-atom reactor experiments support the conclusion that a metal–anhydride complex formed at low temperatures and subsequently decomposed upon warming. Low-temperature argon matrices of all three metal systems contained new bands in the carbonyl stretching region which were significantly different from those reported for any of the metal trifluoroacetates [4, 8, 9]. The palladium and nickel spectra at 12 °K contained doublets at 1625, 1605 and 1640, 1618 cm^{-1} respectively which coalesced to one peak at 1625 cm^{-1} upon warming to 35 K. We believe that this was probably the result of a matrix-site splitting effect, as seen in other matrix isolation experiments [5], although it was not confirmed here. The broad, weak band at 1738 cm^{-1} in the nickel spectrum that was not found in other nickel experiments is unexplained. Of the three metals used in these experiments, copper reacted to form the most intense new absorption in the carbonyl region at 1635 cm^{-1}.

We believe that it is reasonable to assign the new bands in each of these experiments at 12 K to a metal–anhydride complex, as opposed to a decomposition product, since the amount of

anhydride decomposing from oven radiation was found to be small based on the increase in CO and CO$_2$ concentrations in the matrix. Furthermore, no indication was found for a hydrolysis reaction with trace amounts of water in the matrix at these temperatures during deposition or warming periods. The stoichiometries of these complexes are uncertain at this point, although we believe they are 1:2/metal: anhydride, based on the similarity of results obtained in all three reactions and the formation of bis-trifluoroacetate complexes upon decomposition in the palladium and nickel reactions. Additional experimental work involving metal–ligand concentrations and isotopic labeling would be necessary to confirm this.

Warming experiments, whose results are summarized in Table III, revealed distinct differences in the thermal stabilities of these complexes. For example, in the palladium system, no changes were observed in the carbonyl stretching region of the infrared spectrum at temperatures up to −20 °C. Above this temperature the bands were too poorly defined to determine their positions. Since the residues from synthetic-scale reactions released unreacted TFAA upon standing at ambient conditions and formed ether solutions that slowly deposited palladium black, the spectrum of the residue on the window at −20 °C after removal of the excess TFAA (Fig. 2b) would appear to be that of the palladium–anhydride complex.

A similar behavior was observed in the warm-up of the Ar/TFAA matrix containing copper atoms. The band at 1635 cm^{-1}, which was formed at 12 K, broadened and overlapped the one at 1580 cm^{-1} between 60 and 65 K. No further changes were seen in this region until warming above −15 °C, when the band at 1635 cm^{-1} was replaced by bands at 1690 and 1667 cm^{-1} as shown in Fig. 3c. As in the palladium reaction, it is likely that the spectrum of the residue at −15 °C in Fig. 3b is that of the copper–anhydride complex, whereas that at room temperature could be either the copper(I) or copper-(II) trifluoroacetate complex based on the reasonable agreement with both [8–10].

Warming the matrix containing nickel atoms, however, produced some very different results. In the temperature range of 70 K after removal of the argon, an intense broad band at 1660 cm^{-1} and a weaker one at 1460 cm^{-1} were seen replacing the band at 1625 cm^{-1} in the carbonyl region. Further warming to ambient conditions produced no additional changes in the spectrum which is shown in Fig. 4b. The similarity of this spectrum with that reported for Ni(O$_2$CCF$_3$)$_2$ [4] leads us to conclude that the residue was the nickel(II) trifluoroacetate complex.

The order of stability of the anhydride complexes suggested in these experiments, Ni < Cu < Pd, is

also the same as that of the metal ionization potentials (Ni = 7.63 ev, 175.6 kcal; Cu = 7.72 ev, 177.6 kcal; Pd = 8.33 ev, 191.6 kcal) and may be the result of the ease with which the metal atoms undergo oxidation by TFAA.

The implication from matrix isolation work that metal–anhydride complexes were formed at low temperatures received considerable support from results of synthetic scale experiments using the metal atom reactor. The basis for this support rested primarily on the unreacted TFAA that was removed from the reactor above −45 °C in both the palladium (1.07 mmol) and copper (1.29 mmol) systems. The suggestion here was that a metal–TFAA complex formed at low temperatures and then released some of the TFAA unchanged upon warming. The collection of a significantly smaller amount of TFAA (0.20 mmol) under the same conditions in the nickel reaction was also consistent with the observation from matrix isolation experiments that the nickel–anhydride complex was much less stable than that of palladium or copper and decomposed at a lower temperature.
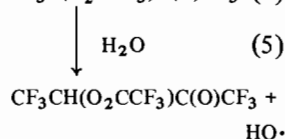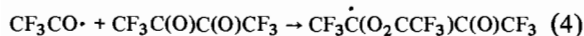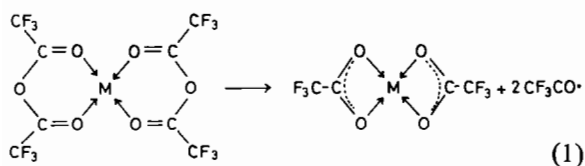
Several volatile products that were isolated or detected in these reactions require comment. Small quantities of CF_3COF were isolated at −45 °C in the palladium (0.09 mmol) and copper (0.08 mmol) systems, whereas a significantly larger amount was isolated in the nickel reaction (0.33 mmol). We feel that the thermal decomposition of trace amounts of the anhydride could give rise to the CF_3COF in the palladium and copper systems, but that this explanation could not satisfactorily account for the larger quantities found in the nickel reaction. Consequently, we conclude that most of the CF_3-COF in the latter case arose from decomposition of a nickel–TFAA complex as shown in equations (1) and (2) of Scheme 1. In the copper system, which appeared to be of intermediate stability, we found

that above −45 °C, CF_3COF (0.03 mmol) and the keto ester $CF_3CH(O_2CCF_3)C(O)CF_3$ (0.27 mmol) were recovered in addition to the TFAA. This suggested that the copper–TFAA complex was starting to decompose at this temperature and that the initial decomposition products, particularly the CF_3CO radical, were reacting differently than in the nickel system. One interpretation of this is shown in Scheme 1 where equations (3) and (4) are similar to those proposed by Filatov and Englin for the $Fe(CO)_5$–TFAA system [6]. Although the vacuum system was rigorously dried prior to the reaction, trace quantities of water indicated in equation (5) would not be unexpected due to small leaks in the system over extended periods of time. A final volatile product of note is the trace quantity of $Ni(CO)_4$ observed in the nickel system. This is believed to originate from the reaction of nickel atoms with CO produced from the oven and from the thermal decomposition of small quantities of TFAA. Other products of the TFAA decomposition, as reported by Corbet and Whittle [7] for pyrolysis below 260 °C, would be CO_2 and CF_3COF, both of which are identified in this system.

The solid products from these reactions were not identified completely in all cases, but the evidence suggested that they were metal trifluoroacetates. Klabunde and coworkers used Et_3P to isolate $(Et_3P)_2Pd(O_2CCF_3)$ in their work [1], and $Fe(O_2CCF_3)_3$ has been obtained from the reaction of $Fe(CO)_5$ with TFAA [6].

In our experiments, only $Ni(O_2CCF_3)_2$ was identified conclusively as a reaction product in the Ni + TFAA and $Ni(CO)_4$ + TFAA system. In both the palladium and copper synthetic-scale reactions, the differences in frequency of the primary carbonyl stretching vibration from those reported in the literature for the palladium [8] and copper trifluoroacetates [4, 9, 10] made identification on this basis questionable. This is not surprising since it has been pointed out that the positions of these bands will depend upon several factors, including the type of bonding by the ligand to the metal, *viz.* mono *vs.* bidentate *vs.* bridging, the oxidation state and environment of the central atom, and the sampling technique [11, 12].

From results of the spectroscopic and synthetic experiments described above, we have concluded that palladium, copper, and nickel atoms reacted initially with TFAA at low temperatures to form intermediate, low-valent metal complexes. The palladium complex decomposed near room temperature to regenerate palladium metal, TFAA, and formed small amounts of $Pd(O_2CCF_3)_2$; copper and nickel formed similar, but less stable, complexes. The copper complex decomposed above −45 °C to give TFAA, a solid believed to be a trifluoroacetate complex, and small quantities of other

$$CF_3CO\cdot + F \rightarrow CF_3COF \tag{2}$$

$$CF_3CO\cdot + CF_3CO\cdot \rightarrow CF_3C(O)C(O)CF_3 \tag{3}$$

$$CF_3CO\cdot + CF_3C(O)C(O)CF_3 \rightarrow CF_3\overset{\cdot}{C}(O_2CCF_3)C(O)CF_3 \tag{4}$$

$$\Big\downarrow H_2O \tag{5}$$

$$CF_3CH(O_2CCF_3)C(O)CF_3 +$$

Scheme 1 $\qquad\qquad\qquad\qquad HO\cdot$

decomposition products. The nickel complex, on the other hand, decomposed below liquid nitrogen temperatures to yield mainly $Ni(O_2CCF_3)_2$ and CF_3-COF. A second source of low-valent nickel, $Ni(CO)_4$, also reacted with TFAA to yield essentially the same products.

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