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Oxidative Displacement and Addition Reactions of *F-tert*-Butyl Hypochlorite with Metal Chlorides and Oxidative Additions to Several Elements

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Transition-metal and post-transition-metal chlorides underwent oxidative displacement and oxidative addition reactions with *F-tert*-butyl hypochlorite to form new *F-tert*-butoxides. Thus, when $(CF_3)_3COCl$ was reacted with $VOCl_3$, $TiCl_4$, and CrO_2Cl_2, the stable compounds $VO[(CF_3)_3CO]_3$, $Ti[(CF_3)_3CO]_4$, and $CrO_2[(CF_3)_3CO]_2$ were formed. With Vaska's compound, oxidative addition occurred at iridium but the phenyl groups of $P(C_6H_5)_3$ were also involved. UCl_4, Cu_2Cl_2, $SnCl_4$, and $SiCl_4$ did not react under the experimental conditions used. *F-tert*-Butyl hypochlorite has also been shown to add oxidatively to such elements as sulfur, lead, tellurium, bismuth, and iodine to form $S[(CF_3)_3CO]_4$, $Pb[(CF_3)_3CO]_2$, $Te[(CF_3)_3CO]_4$, $Bi[(CF_3)_3CO]_3$, and $I[(CF_3)_3CO]_3$, respectively. With $(C_2H_5)_2NH$, $(CF_3)_3COH$ formed a 1:1 adduct.

Introduction

The behavior of *F-tert*-butyl hypochlorite as a reactant under mild conditions continues to provide a route to new nonmetal and metal *F-tert*-butoxides. Recently its ability to behave as a reagent whose reaction mode is oxidative addition, oxidative displacement, or oxidative displacement and oxidative addition has been demonstrated with a variety of non-metal systems, e.g., BCl_3,[2] PCl_3,[3] PCl_5,[3] $PClF_4$,[4] PCl_2F_3,[4] $\overline{S(CF_2)_2S}$,[5] SCl_2,[5] $CF_3S(O)Cl$,[5] and S_4N_4.[6] We now report our studies that deal with its reactions with transition-metal chlorides and some post-transition-metal chlorides as well as with certain elements. Although the decomposition of *F-tert*-butyl hypochlorite into $(CF_3)_2CO + CF_3Cl$ appears to be enhanced in the presence of some metal compounds, it is possible to prepare relatively volatile metal *F-tert*-butoxides in acceptable yields by carefully controlling the reaction conditions.

Results and Discussion

The vanadyl complex $VO[(CF_3)_3CO]_3$ was prepared easily by condensing $(CF_3)_3COCl$ onto $VOCl_3$. The reaction occurred readily at 0 °C to give the product in quantitative yield.

$$3(CF_3)_3COCl + VOCl_3 \xrightarrow{0\ ^{\circ}C} VO[(CF_3)_3CO]_3 + 3Cl_2$$

After sublimation, the new vanadyl complex is a colorless crystalline solid that melts at 62–63 °C. Although no molecular ion was observed in the mass spectrum, appropriate fragments result from the *F-tert*-butoxy groups that are present. The ^{19}F NMR spectrum has a single resonance band at ϕ −73.3.

When *F-tert*-butyl hypochlorite was reacted with $TiCl_4$ at 0 °C, the yield of pure titanium(IV) *F*-alkoxide was nearly quantitative. After sublimation it is a colorless solid that melts at 126 °C.

$$4(CF_3)_3COCl + TiCl_4 \xrightarrow{0\ ^{\circ}C} Ti[(CF_3)_3CO]_4 + 4Cl_2$$

The structure of this compound is supported by its spectral data. The $(M{-}F)^+$ fragment was observed as the highest mass peak in the mass spectrum. The ^{19}F NMR spectrum has a resonance band at ϕ −74.6. The *F*-alkoxide is stable up to 200 °C. An attempt to prepare $Ti[(CF_3)_3CO]_4$ via the reaction of $(CF_3)_3COH$ with $TiCl_4$ was unsuccessful. However, by addition of diethylamine to this mixture a reaction occurred readily even at a low temperature to produce a white solid which is soluble in Freon-11. The ^{19}F NMR spectrum contained major resonance bands at ϕ −72.7, −74.6, and −76.3. The NMR band at ϕ −74.6 is likely due to the presence of $Ti[(CF_3)_3CO]_4$ in the mixture. It was found that the major resonance band at ϕ −76.3 was due to the $(CF_3)_3COH{\cdot}(CH_3CH_2)_2NH$ complex. This diethylamine complex is a white solid that is easily prepared by reacting $(CF_3)_3COH$ with $(CH_3CH_2)_2NH$. It is of interest to compare this amine–alcohol complex with that formed between diethylamine and bis(trifluoromethyl)hydroxylamine, $(CF_3)_2NOH$, under essentially the same conditions.[7] The complex isolated was the 1:2 adduct, $(C_2H_5)_2NH{\cdot}[(CF_3)_2NOH]_2$ (mp 41.5–42.5 °C), and since the hydroxylamine is much less acidic ($pK_a = 8.2$) than $(CF_3)_3COH$ ($pK_a = 5.2$), it is not surprising that partial dissociation to the components is observed in the gas-phase infrared spectrum of the 1:2 adduct. This partial dissociation did not occur for the *F-tert*-butyl alcohol adduct. The solid-phase infrared spectra of these two adducts are similar in that no well-defined peaks are observed in the N–H and C–H regions, but rather there are broad, weak bands covering the region 2400–3000 cm^{-1}, probably due to N–H vibrations.

While it appears possible to prepare some *F-tert*-butoxy derivatives by use of the alcohol and a base or with sodium *F-tert*-butoxide,[8,9] the hypochlorite method produces fewer side products and is relatively stable with other strong oxidizing systems with $(CF_3)_2CO$, CF_3Cl, and Cl_2 as the only side products being formed.

The reaction of $(CF_3)_3COCl$ with CrO_2Cl_2 required warming above 0 °C to ensure complete reaction. The product, $CrO_2[(CF_3)_3CO]_2$, was formed in nearly quantitative yield.

$$(CF_3)_3COCl + CrO_2Cl_2 \rightarrow CrO_2[(CF_3)_3CO]_2 + 2Cl_2$$

The new chromyl compound is a thermally stable orange-red liquid that is sensitive to light. In CCl_4, the UV–vis spectrum has two bands at 279 and 402 nm. Other chromyl compounds in CCl_4 gave similar spectra.[10] The ^{19}F NMR spectrum has a singlet at ϕ −73.0. Although no molecular ion was observed in the mass spectrum, appropriate fragments resulting from the *F-tert*-butoxy group are present.

Chromyl *F-tert*-butoxide, like the vanadium and titanium derivatives, is extremely water sensitive. With $CrO_2[(CF_3)_3CO]_2$ and water, a yellow chromium(VI) solution and $(CF_3)_3COH$ were produced.

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(1) (a) Portland State University. (b) Visiting Professor on leave from Portland State University, 1982. (c) University of Idaho.

(2) Young, D. E.; Anderson, L. R.; Fox, W. B. *Inorg. Chem.* **1971**, *10*, 2810.

(3) Mir, Q. C.; Shreeve, R. W.; Shreeve, J. M. *Phosphorus Sulfur* **1980**, *8*, 331.

(4) Youngs, D. E.; Fox, W. B. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 1033.

(5) Mir, Q. C.; Laurence, K. A.; Shreeve, R. W.; Babb, D. P.; Shreeve, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 5949.

(6) Gard, G. L.; Shreeve, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 5566.

(7) Flaskerud, G. G.; Shreeve, J. M. *Inorg. Chem.* **1969**, *8*, 2065.

(8) Johnson, D. A.; Taylor, J. C.; Waugh, A. B. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 205.

(9) Johnson, D. A.; Waugh, A. B. *J. Fluorine Chem.* **1983**, *22*, 51.

(10) Gerlach, J. N.; Gard, G. L. *Inorg. Chem.* **1970**, *9*, 1565.

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$$CrO_2[(CF_3)_3CO]_2 + 2H_2O \rightarrow [H_2CrO_4] + 2(CF_3)_3COH$$

The formation of $(CF_3)_3COH$ was confirmed by the appearance of its ^{19}F NMR singlet at ϕ −74.9.

While it is known that $(CF_3)_3COCl$ will add oxidatively to free carbon monoxide, its behavior with coordinated carbon monoxide groups was unknown. $(CF_3)_3COCl$ reacts readily with *trans*-$[IrCl(CO)(PPh_3)_2]$ to produce a light yellow solid that when warmed to 150 °C under vacuum turns golden brown. This golden brown solid is insoluble in water but soluble in CCl_3F. Its melting point is 137 ± 2 °C. The ^{19}F NMR spectrum contained two resonance bands at ϕ −69.6 and −70.5 with a relative band area of 3:1, respectively. The ^1H NMR spectrum contained major bands at 7.58, 2.00 and 1.25 ppm. The infrared spectrum contained a band of medium intensity at 2085 cm^{-1}, which is in the region found for carbon monoxide coordinated to an iridium(III) complex.[11] A weak band at 308 cm^{-1} is in the Ir–Cl region. The above data strongly suggest that $(CF_3)_3COCl$ has oxidatively added to iridium(I), giving an iridium(III) complex that is tentatively postulated as $[Ir\{(CF_3)_3CO\}_2Cl(CO)L_2]$ where L is no longer PPh_3 but a complex ligand containing $(CF_3)_3CO$– and Cl– groups. The above NMR studies support a ligand complex with three $(CF_3)_3CO$– groups per PPh_3. Iridium would be bonded to two $(CF_3)_3CO$ groups. It should be pointed out that bis(trifluoromethyl) nitroxide, $(CF_3)_2NO\cdot$, is also capable of oxidizing *trans*-$[IrCl(CO)(PPh_3)_2]$ in CCl_4 to the iridium(III) complex $[Ir\{ON(CF_3)_2\}_2Cl(CO)(PPh_3)_2\cdot CCl_4]$.[12]

F-tert-Butyl nitrite, $(CF_3)_3CONO$, is easily prepared, in nearly quantitative yield, by reacting $(CF_3)_3COCl$ with NOCl at 0 °C.

$$NOCl + (CF_3)_3COCl \xrightarrow{0\ ^\circ C} (CF_3)_3CONO + Cl_2$$

This material was previously prepared[13] by the following sequence:

$$(CF_3)_2C{=}CF_2 + NOF \rightarrow (CF_3)_3C{-}N{=}O \xrightarrow[2\ \text{months}]{NO_2} (CF_3)_3CONO$$

The complete infrared spectrum of this compound is now reported along with its mass spectrum. Although no molecular ion was observed, appropriate fragments resulting from the *F-tert*-butoxy groups as well as the NO^+ ion are present.

The infrared spectra of all new compounds clearly indicate the presence of *tert*-C_4F_9O– groups, with absorption bands in the 1145–1305-cm^{-1} region attributable to the C–F stretching frequency and with bands in the 720–762-cm^{-1} region for the C–F deformation modes. It is likely that the absorption bands around 1000 cm^{-1} are due to the C–O–C stretching vibration. Metal oxygen vibrations (M=O) also occur in this region.

Surprisingly, UCl_4, Cu_2Cl_2, and post-transition-metal chlorides such as $SnCl_4$ and $SiCl_4$ fail to react with $(CF_3)_3COCl$. In all cases, the hypochlorite is decomposed to $(CF_3)_2C{=}O$ and CF_3Cl without reaction.

The halogen-like behavior of $(CF_3)_3COCl$ is particularly evident in its reactions with easily oxidizable elements. For example, just as bismuth and tellurium react at room temperature with an excess of chlorine or $(CF_3)_3NO\cdot$[14] to form BiR_3 and TeR_4 (R = Cl or $(CF_3)_3NO$), these metals react under essentially the same conditions with $(CF_3)_3COCl$ to form $Bi[(CF_3)_3CO]_3$ and $Te[(CF_3)_3CO]_4$, viz.

$$2Bi + 6(CF_3)_3COCl \rightarrow 2Bi[(CF_3)_3CO]_3 + 3Cl_2$$

$$Te + 4[(CF_3)_3COCl] \rightarrow Te[(CF_3)_3CO]_4 + 2Cl_2$$

These compounds are white, crystalline solids that hydrolyze with water to form the parent alcohol. While powdered lead reacts with $(CF_3)_3COCl$ to give $Pb[(CF_3)_3CO]_2$ in essentially quantitative yield, no reaction was found to occur with silicon under any conditions that preclude total hypochlorite decomposition.

Although the behavior of $(CF_3)_3COCl$ and $(CF_3)_2NO\cdot$ with metal halides and metals is essentially identical, their respective reactions with sulfur and iodine are disimilar. With sulfur, as with all lower valent compounds that contain sulfur, the hypochlorite adds oxidatively to produce a compound that contains sulfur(IV), specifically with $S_8 \rightarrow S[(CF_3)_3CO]_4$.[5] The purple radical, $(CF_3)_2NO\cdot$, oxygenates and oxidatively adds to sulfur to form the same product as obtained with SO_2, i.e., $[(CF_3)_2NO]_2SO_2$, where sulfur exists as S^{VI}. There are no examples where $(CF_3)_3COCl$ reacts with sulfur compounds to oxidize sulfur from a lower oxidation state to sulfur(VI) with the exception of the oxidative addition to SO_2 to form $(CF_3)_3COSO_2Cl$. There is no evidence for the *tert*-butyl hypochlorite behaving as an oxygenating reagent.

With iodine, an excess of $(CF_3)_3COCl$ reacts to form the orange iodine(III) compound, $I[(CF_3)_3CO]_3$, in 97% yield under mild reaction conditions. In sharp contrast, no isolable compound is formed between iodine and $(CF_3)_2NO\cdot$, although traces of iodine catalyzed the reactions of the radical with certain less reactive halides.[14] It should be noted that even when a large excess of hypochlorite was used in the reaction with iodine, no evidence for I^V was found. The orange solid sublimes slowly at 25 °C to form a crystalline material.

One of the drawbacks in using $(CF_3)_3COCl$ with oxidizable compounds is its relatively low stability. Reactions must be run routinely at 0 °C or below to prevent rather rapid thermal decompoistion of the hypochlorite. It is also easily decomposed by ultraviolet radiation. Thus, only the mildest conditions may be employed in the study of its chemistry.

A UV–vis spectrum of *F-tert*-butyl hypochlorite in perfluoro-2-butyltetrahydrofuran was obtained on a Cary 14 spectrophotometer. The λ_{max} occurred at 256 nm; other organic hypochlorites give similar spectra.

Experimental Section

Materials. The compounds used in this work were obtained from commercial sources: $(CF_3)_3COH$ and $TiCl_4$ (PCR), CrO_2Cl_2 (treated with mercury and vacuum distilled), Cu_2Cl_2, $SbCl_5$, $TiCl_4$, and $VOCl_3$ (Alfa), NOCl, and UCl_4 (ROC/RIC), $SnCl_4$, CCl_4 (Baker), $(CH_3CH_2)_2NH$, Te, Pb, Si, and I_2 (Mallinckrodt), and S_8 (MCB). Except for CrO_2Cl_2, they were used without further purification. *F-tert*-Butyl hypochlorite was synthesized by the literature method.[15] We are indebted to Dr. M. Roundhill for a gift of *trans*-$[IrCl(CO)(PPh_3)_2]$.

General Procedure. Gases were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge and a Televac thermocouple gauge. Infrared spectra were obtained by using a 5-cm stainless steel cell with KBr windows or as solids between KBr disks on a Perkin-Elmer 599 spectrometer. ^{19}F NMR spectra were recorded with a JEOL FX90Q spectrometer operating at 84.26 MHz. Chemical shifts are relative to CCl_3F. Mass spectra were measured with a Hitachi Perkin-Elmer RMU-6E mass spectrometer at 15 eV. The UV–vis spectrum of $CrO_2[(CF_3)_3CO]_2$ was obtained on a Hewlett-Packard 8450A spectrophotometer. Elemental analyses were performed at the University of Idaho or by Beller Laboratories, Göttingen, W. Germany.

$VOCl_3$ with $(CF_3)_3COCl$. To a 75-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.677 mmol of $VOCl_3$ and 2.73 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (22 h). After the volatile materials were removed under vacuum, the light yellow solid, $VO[(CF_3)_3CO]_3$ (0.670 mmol), was formed in 99% yield. Separation and analyses of the volatile material found $(CF_3)_2CO$, CF_3Cl, and Cl_2 (2.05 mmol,

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(11) Collman, J. P.; Roper, W. R. *Adv. Organomet. Chem.* **1968**, *7*, 53.

(12) Booth, B. L.; Haszeldine, R. N.; Holmes, R. G. *J. Chem. Soc., Dalton Trans.* **1982**, 52.

(13) Andreades, S. *J. Org. Chem.* **1962**, *27*, 463.

(14) Babb, D. P., Shreeve, J. M. *Intra-Science Chem. Rep.* **1971**, *5*, 55.

(15) Gould, D. E.; Anderson, L. R.; Young, D. E.; Fox, W. B. *J. Am. Chem. Soc.* **1970**, *92*, 2313.

theoretical yield 2.03 mmol). The light yellow product sublimed in vacuo at ~60 °C to a white crystalline solid, mp 62–63 °C. The infrared spectrum of $VO[(CF_3)_3CO]_3$ shows bands (cm^{-1}) at 1300 (s), 1265 (s, b), 1192 (m), 1140 (s, b), 1044 (w), 977 (s), 847 (ms), 810 (sh), 760 (vw), 753 (w), 727 (s). The ^{19}F spectrum contained a singlet at −73.3 ppm.

Anal. Calcd: C, 18.67. Found: C, 17.71.

$TiCl_4$ with $(CF_3)_3COCl$. To a 200-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 1.40 mmol of $TiCl_4$ and 6.83 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (18.5 h); an additional 1.62 mmol of $(CF_3)_3COCl$ was added and again the mixture was maintained at 0 °C (41.5 h). After the volatile materials were removed under vacuum, the white solid, $Ti[(CF_3)_3CO]_4$ (1.35 mmol), was obtained (96% yield). Separation and analyses of the volatile material showed $(CF_3)_2CO$, CF_3Cl, and Cl_2 (5.1 mmol, theoretical yield 5.6 mmol). The white solid sublimes at ~50 °C under vacuum; mp 126 °C.

The infrared spectrum of $Ti[(CF_3)_3CO]_4$ shows bands (cm^{-1}) at 1305 (m), 1255 (s, b), 1194 (m), 1150 (s, b), 1085 (sh), 986 (s), 858 (m), 736 (s), 583 (w), 562 (w), 550 (m), 415 (m). The ^{19}F NMR spectrum contained a singlet at −74.6 ppm. A molecular ion was not observed, but other appropriate fragment ions were found: *m/e* 969 $(M - F)^+$, 919 $(M - CF_3)^+$, 753 $[M - (CF_3)_3CO]^+$, 684 $[M - (CF_3)_3CO - CF_3]^+$, 615 $[M - (CF_3)_3CO - 2CF_3]^+$, 518 $[M - 2(CF_3)_3CO]^+$, 197 $[(CF_3)_3CO - 2F]^+$, 178 $[(CF_3)_3CO - 3F]^+$, 147 $[(CF_3)_2CO - F]^+$, 97 $(CF_3CO)^+$, 69 $(CF_3)^+$. Fragment ions with titanium present were a multiplet.

Anal. Calcd: Ti, 4.82; C, 19.45; F, 69.2. Found: Ti, 5.00; C, 18.56; F, 69.3.

$TiCl_4$ with $(CF_3)_3COH$. To a 200-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 0.7822 mmol of $TiCl_4$ and 3.573 mmol of $(CF_3)_3COH$. The reaction mixture was maintained at room temperature (18 h) and then heated to 30–50 °C (7.5 h). No reaction was evident, and an infrared spectrum showed essentially $(CF_3)_3COH$ and no HCl.

$TiCl_4$ with $(CF_3)_3COH$ and $(CH_3CH_2)_2NH$. To the above reaction mixture was added 3.114 mmol of $(CH_3CH_{22}NH$. A yellowish white solid was formed as the reaction mixture was warmed slowly from −196 to 0 °C. After 20 h at 0 °C the volatile materials were removed, leaving behind 1.1498 g of a light yellow solid. The ^{19}F NMR spectrum of the solid in Freon-11 gave the major resonance bands at ϕ −72.7, −74.6, and −76.3. Since the solid contained several different compounds, further studies were discontinued.

$(CF_3)_3COH$ with $(CH_3CH_2)_2NH$. To a 100-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 0.66 mmol of $(CF_3)_3COH$ and 7.4 mmol of $(CH_3CH_2)_2NH$. Upon warming to room temperature a white solid was immediately formed and after 0.75 h at room temperature the volatile materials were removed, leaving behind a sublimable white solid [0.62 mmol of $(CF_3)_3COH\cdot(CH_3CH_2)_2NH$], yield 94%; mp 159 ± 2 °C.

The infrared spectrum of $(CF_3)_3COH\cdot(CH_3CH_2)_2NH$ shows bands (cm^{-1}) at 3038 (w), 2996 (m), 2952 (m), 2918 (wm), 2868 (wm), 2600 (vb, m), 1656 (sh), 1648 (m), 1502 (m), 1480 (m), 1458 (m), 1394 (m), 1376 (m), 1290 (sh), 1256 (s), 1220 (b, s), 1172 (s), 1150 (sh), 1064 (m), 1050 (m), 1014 (w), 956 (s), 866 (w), 822 (s), 758 (w), 720 (s), 668 (w).

The ^{19}F NMR spectrum contained a singlet at −76.3 ppm. The ^1H NMR spectrum gave a broad singlet at 10.10 ppm, a quartet at 2.74 ppm, and a triplet at 1.34 ppm; the relative peak areas were NH (2.0), CH_2 (4.0), and CH_3 (6.0).

Anal. Calcd: C, 31.07; H, 3.92; N, 4.53. Found: C, 30.83 H, 3.93; N, 4.65.

CrO_2Cl_2 with $(CF_3)_3COCl$. To a 200-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 1.18 mmol of CrO_2Cl_2 and 3.65 mmol of $(CF_3)_3COCl$. The reaction mixture was warmed to 0 °C and then to room temperature (1.8 h); an additional 2.12 mmol of $(CF_3)_3COCl$ was added and the mixture maintained at 0 °C (66 h). The volatile materials at −44 °C were separated and analyzed; $(CF_3)_2CO$, CF_3Cl, Cl_2 (2.35 mmol, theoretical yield 2.36 mmol) were found. The nonvolatile material left behing at −44 °C was an orange-red liquid, $CrO_2[(CF_3)_3CO]_2$, 1.12 mmol; yield 95%.

The gaseous infrared spectrum of $CrO_2[(CF_3)_3CO]_2$ shows bands (cm^{-1}) at 1305 (m), 1272 (s, b), 1198 (vw), 1180 (vw), 1167 (sh), 1145 (s), 1000 (m), 985 (ms), 837 (w), 732 (m), 542 (w). The ^{19}F NMR spectrum contained a singlet at −73.0 ppm. Addition of water to a sample of $CrO_2[(CF_3)_3CO]_2$ produced $(CF_3)_3COH$, as identified by its characteristic NMR resonance at ϕ −74.9 and a yellow oxidizing solution of H_2CrO_4. The UV–vis spectrum of the compound in CCl_4 contained two bands at 279 and 402 nm.

Anal. Calcd: Cr, 9.39; C, 17.35. Found: Cr, 9.38; C, 16.82.

NOCl with $(CF_3)_3COCl$. To a 200-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 2.64 mmol of NOCl and 3.59 mmol of $(CF_3)_3COCl$. The reaction mixture was slowly warmed to 0 °C (20 h). Trap-to-trap separation gave 2.48 mmol of $(CF_3)_3CONO$, yield 94%, and 2.53 mmol of Cl_2 (theoretical yield 2.64 mmol).

The gaseous infrared spectrum of $(CF_3)_3CONO$ shows bands (cm^{-1}) at 1810 (s), 1305 (s), 1288 (vs), 1264 (s), 1210 (w), 1190 (w), 1160 (m), 1132 (m), 1008 (m), 986 (m), 960 (w), 797 (w), 762 (m), 734 (m), 648 (m), 545 (w), 523 (w). The ^{19}F NMR spectrum contained a singlet at −70.9 ppm. A molecular ion was not observed, but other appropriate fragment ions were found: *m/e* 197 $[(CF_3)_3CO - 2F]^+$, 166 $[(CF_3)_2CO]^+$, 147 $[(CF_3)_2CO - F]^+$, 128 $[(CF_3)_2CO - 2F]^+$, 97 $(CF_3CO)^+$, 69 $(CF_3)^+$, $30(NO)^+$.

***trans*-$[IrCl(CO)(PPh_3)_2]$ with $(CF_3)_3COCl$.** To a ~50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.1188 mmol of *trans*-$[IrCl(CO)(PPh_3)_2]$ and 3.16 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (25 h). After the volatile materials were removed under vacuum a yellow solid was left behind. An attempt to sublime this material at temperatures up to 150 °C produced a crystalline golden-yellow solid, mp 137 ± 2 °C. It is soluble in Freon-11 but insoluble in H_2O. The infrared spectrum shows bands (cm^{-1}) at 3080 (w), 2085 (m), 1620 (w), 1570 (mw), 1545 (sh), 1440 (mw), 1409 (m), 1385 (sh), 1368 (w), 1265 (vs, br), 1186 (s), 1143 (s, br), 1105 (s), 1006 (s), 973 (s), 885 (w), 841 (w), 882 (w), 809 (w), 773 w), 742 (s), 731 (s), 690 (w), 620 (w), 546 (mw), 405 (w), 333 (w), 308 (w).

The ^{19}F NMR spectrum contains two resonance bands at −69.6 and −70.5 ppm, with a relative band area of 1:3, respectively. The ^1H NMR spectrum has major resonance bands at 7.58, 2.00, and 1.25 ppm.

Anal. Calcd for $IrCl_9(CO)[(CF_3)_3CO]_8(PPh_3)_2$: P, 2.16; C, 28.84; H, 1.06; F, 47.62. Found: P, 2.65; C, 28.38; H, 1.12; F, 48.60.

$SnCl_4$ with $(CF_3)_3COCl$. To a 200-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 0.422 mmol of $SnCl_4$ and 2.57 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (9 h) and then at room temperature for 48 h. No solid product was formed, and in the gas phase only the decomposed $(CF_3)_3COCl$ products were observed [$(CF_3)_2C{=}O$ and CF_3Cl].

$SiCl_4$ with $(CF_3)_3COCl$. To a 200-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 0.409 mmol of $SiCl_4$ and 3.3 mmol of $(CF_3)_3COCl$. The reaction mixture was warmed to 0 °C (2.5 h) and then to room ttemperature. No solid/liquid products were formed, and in the gas phase only the decomposed $(CF_3)_3COCl$ products were observed [CF_3Cl and $(CF_3)_2C{=}O$].

UCl_4 with $(CF_3)_3COCl$. To a 200-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 0.654 mmol of UCl_4 and 3.3 mmol of $(CF_3)_3COCl$. The reaction mixture was warmed to 0 °C (120 h). The volatile material contained $(CF_3)_2CO$ and CF_3Cl. The weight of the solid left behind was essentially unchanged.

Cu_2Cl_2 with $(CF_3)_3COCl$. To a 50-mL vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.448 mmol Cu_2Cl_2 and 3.847 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (18 h) and then at room temperature (23 h). The volatile material contained only $(CF_3)_2C{=}O$ and CF_3Cl. The weight of the solid left behind increased only 0.0147 g. The reaction was not studied further.

I_2 with $(CF_3)_3COCl$. To a 200-mL Pyrex-glass vessel equipped with a Kontes Teflon valve were added 0.40 mmol of I_2 and 4.82 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (44 h). After removal of the volatile materials under vacuum, 0.78 mmol of the orange solid, $I[(CF_3)_3CO]_3$, was formed in 97% yield. Separation and analyses of the volatile material found $(CF_2)_3CO$, CF_3Cl, and Cl_2 (1.20 mmol, theoretical yield 1.21 mmol). The product, $I[(CF_3)_3CO]_3$, slowly sublimed at room temperature under vacuum; mp 22.5–23.5 °C.

The infrared spectrum shows bands (cm^{-1}) at 1256 (s, b), 1194 (ms), 1172 (ms), 1144 (s), 1104 (s), 1068 (s), 972 (s), 976 (w), 666 (s), 726 (s), 686 (ms). The ^{19}F NMR spectrum contained a singlet at −72.0 ppm.

Anal. Calcd: C, 17.32; F, 61.65; I, 15.25. Found: C, 17.39; F, 61.3; I, 15.20.

Pb with $(CF_3)_3COCl$. To a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.499 mmol of Pb and 4.50 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (90 h) and at room temperature (50 h); an additional 1.63 mmol of $(CF_3)_3COCl$ was added and again maintained at room temperature (24 h). The materials volatile at −78 °C were periodically removed during this time. The materials volatile at room temperature were removed under vacuum, leaving 0.508 mmol of a light tan solid, $Pb[(CF_3)_3CO]_2$, in ~100% yield. Separation and analysis of the volatile materials found $(CF_3)_2CO$, CF_3Cl, and Cl_2 (0.49 mmol, theoretical yield 0.50 mmol).

The infrared spectrum of $Pb[(CF_3)_3CO]_2$ shows bands (cm^{-1}) at 1304 (ms), 1248 (s, b), 1214 (sh), 1184 (m), 1140 (s), 970 (s), 766 (m), 724 (ms), 674 (w). The ^{19}F NMR spectrum contained a singlet at −74.0 ppm.

Anal. Calcd: C, 14.19. Found: C, 12.81.

Si with $(CF_3)_3COCl$. To a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 0.602 mmol of silicon and 0.933 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (18 h) and then at room temperature (24 h). The volatile material contained only $(CF_3)_2C{=}O$ and CF_3Cl. The weight of the solid left behind increased only 0.0060 g. The reaction was not studied further.

S with $(CF_3)_3COCl$. To a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and a Teflon stirring bar were added 2.59 mmol of sulfur and 3.59 mmol $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (2 h). Separation and analyses of the volatile material found Cl_2 and S_2Cl_2/SCl_2. The white solid left behind was found to be 0.701 mmol of $S[(CF_3)_3CO]_4$ which was formed in 78% yield. Melting point and spectral data agree with literature values.[5]

Te with $(CF_3)_3COCl$. To a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.429 mmol of Te and 3.67 mmol of $(CF_3)_3COCl$. The reaction mixture was maintained at 0 °C (100 h), at room temperature (90 h), and between 25 and 30 °C (2 h); an additional 1.08 mmol of $(CF_3)_3COCl$ was added and the reaction again maintained at room temperature (24 h). The materials volatile at −78 °C were periodically removed during this time. The materials volatile at room temperature were removed under vacuum, leaving 0.385 mmol of the white solid, $Te[(CF_3)_3CO]_4$, in 90% yield. Separation and analysis of the volatile materials found $(CF_3)_2CO$, CF_3Cl, and Cl_2 (0.85 mmol, theoretical yield 0.86 mmol). The new compound sublimes in vacuo at 70 °C and melts in a sealed tube at 94 ± 1 °C.

The infrared spectrum of $Te[(CF_3)_3CO]_4$ shows bands (cm^{-1}) at 1308 (sh), 1260 (s), 1172 (m), 968 (ms), 760 (sh), 724 (s), 626 (vs, b). The ^{19}F NMR spectrum contained a singlet at −72.1 ppm.

Anal. Calcd: C, 17.99. Found: C, 17.17.

Bi with $(CF_3)_3COCl$. To a 50-mL Pyrex-glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar were added 0.427 mmol of Bi and 1.941 mmol $(CF_3)_3COCl$. Additional amounts of $(CF_3)_3COCl$ were added later (2.86, 3.28, and 0.71 mmol). Cumulatively, the reaction mixture was maintained at 0 °C (40 h), room temperature (94 h), and 25–30 °C (6 h). The materials volatile at −78 °C were removed periodically during this time. The materials volatile at 25 °C were removed under vacuum, leaving 0.40 mmol of the white solid, $Bi[OC(CF_3)_3]_3$, in 93% yield. Separation and analyses of volatile materials found CF_3Cl, $(CF_3)_2C(O)$, $(CF_3)_3COH$, and Cl_2.

The infrared spectrum of $Bi[OC(CF_3)_3]_3$ shows bands (cm^{-1}) at 1303 (ms), 1245 (s), 1207 (sh), 1153 (s), 965 (s), 765 (w), 723 (s). The ^{19}F NMR spectrum contained a singlet at −74.2 ppm.

Anal. Calcd: C, 15.77; F, 56.12. Found: C, 15.45; F, 54.4.

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Registry No. $VO[(CF_3)_3CO]_3$, 88391-96-2; $Ti[(CF_3)_3CO]_4$, 88391-97-3; $CrO_2[(CF_3)_3CO]_2$, 88391-99-5; $Pb[(CF_3)_3CO]_2$, 88392-01-2; $I[(CF_3)_3CO]_3$, 88392-00-1; $S[(CF_3)_3CO]_4$, 71906-37-1; $Te[(CF_3)_3CO]_4$, 88392-02-3; $Bi[(CF_3)_3CO]_3$, 88392-03-4; $(CF_3)_3COH\cdot(CH_3CH_2)_2NH$, 88391-98-4; NOCl, 2696-92-6; $(CF_3)_3COCl$, 27579-40-4; $(CF_3)_3CONO$, 677-88-3; *trans*-$[IrCl(CO)(PPh_3)_2]$, 15318-31-7; I_2, 7553-56-2; Pb, 7439-92-1; S, 7704-34-9; Te, 13494-80-9; Bi, 7440-69-9.

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Cis Effect of the Phosphorus Ligand, L, in Six-Coordinate $Ru(CO)_3(L)(SiCl_3)_2$ Compounds. Importance of the Steric Factor[1]

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The rate of substitution of the equatorial carbonyl by $P(OMe)_3$ has been investigated for 24 different molecules of the type *mer*-$Ru(CO)_3(L)(SiCl_3)_2$ ($SiCl_3$ groups mutually cis; L a phosphorus donor ligand). Detailed studies on the substitution in $Ru(CO)_3(PPh_3)(SiCl_3)_2$ were entirely consistent with a dissociative mechanism for the process. Rates, at 40 °C, vary by $\sim 10^3$ depending on the nature of L. With four exceptions, the activation parameter $\Delta H^{\ddagger}$ was found to be approximately constant for each case. This is interpreted as signifying that ground-state electronic effects are unimportant in determining the differences in rates. In contrast, for these nonexceptional examples, the $\Delta S^{\ddagger}$ values vary from 4 to 19 cal mol^{-1} deg^{-1}. Furthermore, there is a reasonably linear correlation between $\Delta S^{\ddagger}$ and the size of the phosphorus ligand as measured by the cone angle, θ, of L. It is concluded that the origin of the cis effect of L in these complexes is almost entirely steric.

Introduction

The most common mechanism by which metal carbonyl complexes undergo substitution reactions is by the initial dissociation of CO as the rate-determining step.[2] In substituted metal carbonyl compounds it appears for most cases that the CO groups cis to the non-carbonyl substituent are labilized with respect to dissociation.[3] This, of course, is in contrast to ligand-displacement reactions in square complexes where the trans effect is of dominant importance.[4] Brown and co-workers have developed the site-preference model in

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[1] Taken in part from: Chalk, K. L. M.S. Thesis, Simon Fraser University, 1982.

[2] Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.

[3] Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3161.

[4] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980, p 1199.

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