secondary (PH(a) and PH(b) and primary PH_2) phosphine moieties of **9**, respectively. In both **8** and **9** the $^2J(PP)$ values of 24–33 Hz are typical of cis-molybdenum(0)-coordinated phosphines.[27] It is assumed that **8**-PH_2(b) and **9**-PH(b) appear as triplets only because of the close coincidence of the two ^2J coupling constants. That the resonances in **8** and **9** are in fact from secondary (PH) and primary (PH_2) phosphines is confirmed in the $^{31}P-^1H$ coupled spectra. Upon ^1H coupling, the **8**-PH, **9**-PH(a), and **9**-PH(b) resonances are broad doublets and the **8**-PH_2(a), **8**-PH_2(b), and **9**-PH_2 resonances are broad triplets of $^1J(PH)$ approximately equal to 300 and 330 Hz, respectively. Although broad, unresolved, and unassigned resonances in the base lines are seen, these are assumed to be due to traces of higher oligomeric or polymeric products and were not assigned. The possibility that the small well-defined resonance groups at δ −3.4 and −77.1 are due to minor amounts of dimolybdenum species or Markovnikov addition[38] products containing 5-membered C/C/P/Mo/P rings cannot be discounted.

On the basis of the spectral assignments above, the sequence of reactions shown in Figure 4 appears to be the major process that occurs during cyclooligomerization. Initial closure of one C_3P_2Mo ring results in **8**, a species containing a single 6-membered metallaphosphacycle ring. Subsequently, after the second step in cyclization occurs, a coordinated bicyclic system (**9**) begins to appear. Upon formation of the third ring, the final coordinated [12-ane]P_3 macrocycle (**6**) is formed. The reaction occurs in moderately well-defined steps, clearly the result of the metal's causing template cyclization and introducing order into the cyclooligomerization reaction. In the absence of metal coordination $CH_2{=}CHCH_2PH_2$ and $CH_2{=}CHCH_2CH_2PH_2$, under AIBN or photolytically promoted reaction conditions, yield different products in complex reaction mixtures.[44]

The [12-ane]P_3 and [15-ane]P_3 molybdenum complexes **6** and **7** showed (by ^{31}P NMR analysis) no decomposition during heating in toluene at 110 °C. Not surprisingly, both are stable to macrocyclic displacement. Exhaustive treatment of these complexes with Ph_3P, PF_3, KCN, or $P(OMe)_3$ resulted in no reaction. Further studies of ligand displacement in order to obtain the free [12-ane]P_3 and [15-ane]P_3 macrocycles are in progress and will be reported later.

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Supplementary Material Available: Listings of crystal data and refinement details, hydrogen atom coordinates, anisotropic thermal parameters, and least-squares planes (8 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Synthesis of Bis(trifluoromethyl)phenylthallium and Bis(trifluoromethyl)thallium Acetate. Oxidative Trifluoromethylation with Bis(trifluoromethyl)thallium(III) Compounds

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The reaction of $Cd(CF_3)_2$·glyme with $TlPhCl_2$ forms $TlPh(CF_3)_2$, which is isolated in 87% yield after 72 h. If $TlPh(OAc)_2$ is the thallium source, $TlPh(CF_3)_2$ is generated in 2 h; however, the isolated yield is lower because acetate reacts with $Cd(CF_3)_2$·glyme, resulting in CH_3COF. The interaction of $Cd(CF_3)_2$·glyme with $Tl(OAc)_3$ produces $Tl(CF_3)_2OAc$, 46%, within 45 min. The possibility of utilizing (trifluoromethyl)thallium(III) species in oxidative trifluoromethylation reactions was screened by employing several classic low-valent metallic species as substrates. The reaction of elemental mercury was the most informative, yielding $Hg(CF_3)_2$ in 77% yield in glyme but generating a mixture of $HgPh(CF_3)$ and $Hg(CF_3)_2$ when CH_2Cl_2 was the solvent. These results are interpreted by postulating mercury insertion into the Tl–Ph bond, resulting in $PhHgTl(CF_3)_2$, which decomposes to generate $HgPh(CF_3)$. The formation of $Hg(CF_3)_2$ is attributed to the reaction of $HgPh(CF_3)$ with $TlCF_3$.

Introduction

Due in part to the low activation energies commonly associated with their reactions, organometallic compounds of the group 3A (13) elements have long been extensively employed in diverse types of chemical transformations. Examples include hydrometalations, ligand-exchange procedures, and a variety of olefin telomerizations and polymerizations involving reactions of organoboron or organoaluminum compounds. Although less well studied, organothallium reagents are also occasionally utilized in more specialized applications: reactions like aromatic thallations, olefin oxythallations, or cyclopentadienations with TlCp.[1]

In contrast to the diverse and important niche that has been carved out for the perhydroalkyl reagents of the main group 3 (13) elements, surprisingly little is known about the preparation and the properties of the perfluoroalkyl derivatives. For example, only two trifluoromethyl-substituted boranes, CF_3BF_2 and $CF_3B(n\text{-}Bu)_2$, have ever been synthesized.[2,3] Other trifluoromethyl–boron-containing species that have been separated include the two anions $CF_3BF_3^-$ and $(CF_3)_2BF_2^-$.[4,5] Within this group of elements, the sole remaining trifluoromethyl derivatives that have been reported are $Tl(CF_3)_3$ and the trimethylphosphine adduct of that compound, $Tl(CF_3)_3PMe_3$, both derived from the reactions of thallium atoms with CF_3 radicals.[6] The utility of (trifluoromethyl)thallium compounds as reagents remains wholly unexplored.

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Even though the compound CF_3BF_2 has been shown to be thermally stable,[2,3] few perfluoroalkyl derivatives of the group 3A (13) elements have been synthesized. One reason may be a still prevalent feeling that tricoordinate perfluoroalkyl compounds, if formed, would inevitably be prone to decomposition. Presumably, at least by analogy to the (trifluoromethyl)boranes[2] and the (trifluoromethyl)phosphoranes,[7] the initial products of the thermal decomposition would include the metal fluoride and difluorocarbene.[3,6,8]

The specific objectives of this study were to determine whether (trifluoromethyl)thallium(III) compounds could be prepared by standard methodology utilizing $Cd(CF_3)_2$·glyme as the trifluoromethyl source, and then, if possible, to ascertain whether the $Tl(CF_3)$ derivatives formed possessed sufficient thermal stability for their employment as reagents. Since perhaps the most common use of both inorganic and organometallic thallium(III) compounds is in redox reactions, the initial experiments were to involve a preliminary examination of the oxidative transfer (transmetalation) of CF_3 groups from Tl(III) to low-valent easily oxidized metallic species.

Experimental Section

General Procedures. Reactions generating the Tl(III) compounds used as substrates below were all carried out in an efficient fume hood. *Because of the toxic nature of many thallium compounds, rubber gloves were worn throughout this portion of the experimental study.* The syntheses and manipulations of the trifluoromethyl-containing derivatives employed standard vacuum lines and gloveboxes.

Mass spectral data, which are reported for the ^{205}Tl isotope only, are from an HP-5985A spectrometer operating at 20 eV and 200 °C. Each ^{205}Tl-containing ion reported was accompanied by the expected ^{203}Tl isotopomer in the anticipated abundance: natural abundance of ^{205}Tl = 70.5%, of ^{203}Tl = 29.5%. The ^{19}F and ^{1}H NMR spectra were obtained from a Bruker WP-200SY instrument; positive chemical shifts are deshielded from external CF_3COOH or TMS, as appropriate. The nuclear spin, I, of both Tl isotopes is $^1/_2$; the ratio of the magnetic moments, hence the expected ratio of the coupling constants, is 1.0098.

Thallium(III) acetate and $TlCl_3 \cdot 4H_2O$ were obtained from Alfa Inorganics. Phenylboric acid, $RhCl(PPh_3)_3$, $Pd(PPh_3)_4$, TlI, and LiMe (1.6 M) were purchased from Aldrich. All were used as received. Solvents were dried over P_2O_5 or sodium benzophenone ketyl, as appropriate. Bis(trifluoromethyl)cadmium–glyme[9] and bis(trifluoromethyl)mercury[10] were prepared as previously described.

Phenylthallium Dichloride. In a 50-mL flask $TlCl_3 \cdot 4H_2O$, 4.500 g (11.8 mmol), $BPh(OH)_2$, 0.600 g (4.92 mmol), and 10 mL of H_2O were held at 100 °C for ca. 1 min. The resulting white precipitate was filtered, washed with water, and dried under vacuum. Recrystallization from water yielded white needles of $TlPhCl_2$: yield 1.567 g (90%); mp 235 °C dec (lit.[11] mp 235 °C). Proton NMR (DMSO-d_6): δ = 7.2 ppm; J_{Tl-H} = 870, 332, and 112 Hz for the ortho, meta, and para protons of the C_6H_5 ring, respectively.

Phenylthallium Diacetate. Excess AgOAc, 3.0 g, was slowly added to a solution of $TlPhCl_2$, 0.800 g (2.27 mmol), contained in 30 mL of MeOH, and the mixture was stirred for 5 h at ambient temperature. After filtration, removal of the solvent under vacuum yielded $TlPh(OAc)_2$, 0.300 g (33%), a white powder that was identified by mass spectrometry and ^1H NMR spectroscopy.[12]

Dimethylthallium Iodide. To a solution of 6.650 g (46.9 mmol) of CH_3I in 20 mL of Et_2O was added 12.0 g (36.2 mmol) of TlI. Methyllithium, 47.0 mL (75.2 mmol), was added dropwise, and the resulting mixture was stirred magnetically for 1 h. After filtration, slow addition of aqueous HI (3 M) resulted in precipitation of $TlMe_2I$. The solid was collected by filtration, washed with water and then with Et_2O, and dried under vacuum. The yield was 11.50 g (88%). This compound was characterized as follows. ^1H NMR (DMSO-d_6): δ = 0.90 ppm; J_{Tl-H} = 436 Hz. Mass spectrometry (m/e, ion, abundance): 127, I, 0.9%; 142, CH_3I, 3.4%; 205, Tl, 40.3%; 220, $TlCH_3$, 6.0%; 235, $Tl(CH_3)_2$, 100.0%; 332, TlI, 8.6%; 347, $Tl(CH_3)I$, 3.1%; 362, $Tl(CH_3)_2I$, 0.8%.[13]

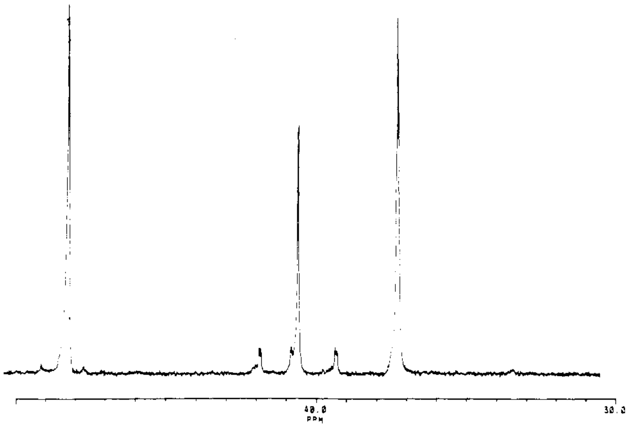

Figure 1. Fluorine NMR spectrum (CH_2Cl_2) of the reaction of $Cd(CF_3)_2$·glyme with $TlPhCl_2$ after 72 h (see text).

Figure 2. Fluorine NMR spectrum of $TlPh(CF_3)_2$.

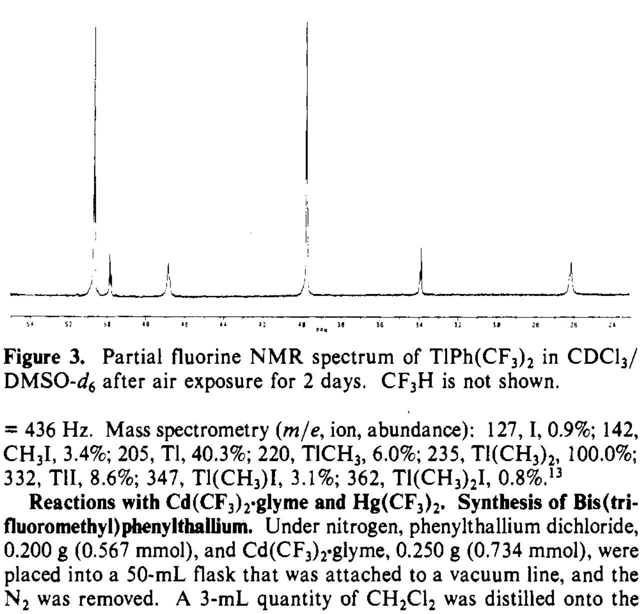

Figure 3. Partial fluorine NMR spectrum of $TlPh(CF_3)_2$ in $CDCl_3$/DMSO-d_6 after air exposure for 2 days. CF_3H is not shown.

Reactions with $Cd(CF_3)_2$·glyme and $Hg(CF_3)_2$. Synthesis of Bis(trifluoromethyl)phenylthallium. Under nitrogen, phenylthallium dichloride, 0.200 g (0.567 mmol), and $Cd(CF_3)_2$·glyme, 0.250 g (0.734 mmol), were placed into a 50-mL flask that was attached to a vacuum line, and the N_2 was removed. A 3-mL quantity of CH_2Cl_2 was distilled onto the reagents, and the mixture was stirred magnetically at ambient temperature. Monitoring of the supernatant by ^{19}F NMR spectroscopy indicated a steady decrease in the intensity of the $Cd(CF_3)_2$·glyme resonance along with a slow but continuous growth of a doublet centered near 43 ppm. Small amounts of CF_3H as well as several other doublets arising from thallium-containing species were also observed during the course of the reaction (see Results and Discussion). After 72 h, ^{19}F NMR spectra of the solution (see Figure 1) indicated the presence of $Cd(CF_3)$ species near 41 ppm along with three Tl-containing compounds present in the relative intensities 0.5:100:2.0.

After the CH_2Cl_2 solution obtained above was briefly exposed to the atmosphere, filtration followed by slow removal of solvent and other

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material volatile at ambient temperature resulted in precipitation of white $TlPh(CF_3)_2$, 0.206 g (87%; see Figure 2).

In $CDCl_3$/DMSO-d_6 the ^{19}F NMR spectrum of this new compound consists of two doublets (δ = 43.9 ppm; $^2J_{Tl-F}$ = 2072 and 2052 Hz). The proton NMR spectrum (δ = 6.6 ppm) contains three sets of resonances (J_{Tl-H} = 592, 194, and 56 Hz) from the ortho, meta, and para protons, respectively. Mass spectrum (*m*/*e*, ion intensity): 69, CF_3, 1.1%; 77, Ph, 1.0%; 205, Tl, 100.0%; 274, $TlCF_3$, 10.0%; 282, TlPh, 8.8%; 343, $Tl(CF_3)_2$, 2.8%; 351, $TlPh(CF_3)$, 7.0%; 401, $TlPh(CF_3)CF_2$, 0.1%. Infrared spectrum (mineral oil): 1462 (w), 1435 (w), 1209 (m), 1101 (vs), 1047 (vs), 850 (m), 688 (w) cm^{-1}.

Although $TlPh(CF_3)_2$ can be routinely handled in the atmosphere, it does slowly react with air. For example, when $TlPh(CF_3)_2$ is dissolved in $CDCl_3$ to which 3 drops of DMSO-d_6 have been added and the mixture is exposed to air for 2 days, resonances of two new $TlCF_3$ compounds, one centered at 41.7 ppm ($J_{^{205}Tl-F}$ = 3008 Hz) and the second at 36.4 ppm ($J_{^{205}Tl-F}$ = 3906 Hz), appear in the ^{19}F NMR spectrum along with resonances of CF_3H (δ = –0.5 ppm; J_{HF} = 80 Hz; see Figure 3). After 2 days more, a third resonance (δ = 36.0 ppm; $^2J_{Tl-F}$ = 5220 Hz) is found. After 10 days, $TlPh(CF_3)_2$ is no longer observed.

Alternative Synthesis of $TlPh(CF_3)_2$. Phenylthallium diacetate, 0.078 g (0.195 mmol), and $Cd(CF_3)_2$·glyme, 0.080 g (0.235 mmol), were stirred in 3 mL of CH_2Cl_2 for 2.0 h at ambient temperature, generating a colorless supernatant and a tan residue. The ^{19}F NMR spectrum of the supernatant contained a large quartet arising from CH_3COF (δ = 127 ppm; J_{H-F} = 7.0 Hz), strong resonances from $TlPh(CF_3)_2$ (δ = 43 ppm), and a small doublet due to CF_3H (δ = –0.5 ppm); $Cd(CF_3)$ species were unobserved. The mixture was briefly exposed to air and filtered, and then the volatile material was slowly removed from the filtrate, resulting in $TlPh(CF_3)_2$, 0.036 g. The yield, based upon the amount of $TlPh(CO_2CH_3)_2$ taken, was 44%. The properties of the compound prepared via this reaction are as reported above.

Synthesis of $Tl(CF_3)_2OAc$. Under N_2, $Tl(OAc)_3$, 0.200 g (0.524 mmol), and $Cd(CF_3)_2$·glyme, 0.500 g (1.47 mmol), were placed in a 25-mL Pyrex reactor. The vessel was attached to a vacuum line and cooled to –196 °C, and, after evacuation, 3 mL of CH_2Cl_2 was distilled onto the mixture. After warming to ambient temperature, the reactor contents were stirred magnetically, resulting in a yellow solid and a pale yellow supernatant. Aside from resonances associated with $Cd(CF_3)_2$·glyme, fluorine NMR spectra of the solution contained very large resonances at 127 ppm (CH_3COF) and –0.5 ppm (CF_3H) in addition to those of three thallium-containing species. The latter resonances were centered at 43.9 ppm (J_{Tl-F} = 2071 Hz), 42.5 ppm (J_{Tl-F} = 2986 Hz), and 39.8 ppm (J_{Tl-F} = 5103 Hz). After 0.75 h, 3 mL of CH_2Cl_2 was added to the solution, and the mixture was filtered through a sintered-glass funnel.

If additional $Cd(CF_3)_2$·glyme was added to the solution at this point, no new resonances were observed in the fluorine NMR spectrum although the intensity of the resonance centered at 42.5 ppm did decrease by a factor of 5 relative to the intensity of the peak centered at 43.9 ppm.

Alternatively, if the solution was briefly exposed to the atmosphere and filtered and the solvent removed under vacuum, a cream-colored powder, $Tl(CF_3)_2OAc$ (0.97 g), was obtained, 46% yield based upon thallium acetate.

Occasionally $Tl(CF_3)_2OAc$, prepared as above, may be slightly (ca. 5%) contaminated by a second thallium-containing compound (δ = 42.5 ppm; J_{Tl-F} = 2986 Hz), which is most readily removed by dissolution in $CHCl_3$ followed by air oxidation of the second, more reactive component. The ^{19}F NMR spectrum of the new compound, bis(trifluoromethyl)thallium acetate, in CH_2Cl_2 consists of two doublets ($^2J_{Tl-F}$ = 2068 and 2049 Hz), which are centered at 42.6 ppm. The ^1H NMR spectrum contains a singlet (1.60 ppm). Mass spectrum: (*m*/*e*, ion, intensity); 69, CF_3, 4.0%; 205, Tl, 100%; 220, $TlCH_3$, 1.2%; 249, $TlCO_2$, 11.0%; 264, $TlCO_2CH_3$, 1.4%; 274, $TlCF_3$, 14.9%; 289, $Tl(CF_3)(CH_3)$, 7.0%; 333, $Tl(OAc)(CF_3)$, 18.7;% 343, $Tl(CF_3)_2$, 30.4%. Infrared absorptions (KBr): 2924 (s), 2853 (m), 2362 (w), 1522 (vs), 1142 (vs), 1109 (vs), 954 (w), 727 (m), 681 (m) cm^{-1}.

Interaction of $TlMe_2I$ with $Cd(CF_3)_2$·glyme. Under N_2, 0.050 g of $TlMe_2I$ and 0.08 g of $Cd(CF_3)_2$·glyme were introduced into a 4-mm Pyrex glass reactor, which was sealed after the addition of glyme, $CH_3OCH_2CH_2OCH_3$ (ca. 2 mL). After 30 days, at ambient temperature, aside from a trace of CF_3H at –0.5 ppm, only unreacted $Cd(CF_3)_2$·glyme had been observed by ^{19}F NMR spectroscopy. Similar results were obtained when diethyl ether or CH_2Cl_2 was employed as solvent.

Exposure of $Tl(OAc)_3$, $TlPh(OAc)_2$, and $PhTlCl_2$ to $Hg(CF_3)_2$. Freshly sublimed $Hg(CF_3)_2$, 0.148 mmol, was placed into each of three 4-mm Pyrex tubes into which 0.052 mmol of one of the compounds $Tl(OAc)_3$, $TlPh(OAc)_2$, or $TlPhCl_2$ was added. After evacuation and the addition of ca. 1 mL of CH_2Cl_2, the vessels were sealed, and the mixtures were examined by ^{19}F NMR spectroscopy over the course of 60 days at ambient temperature. No reaction was detected.

Oxidative Trifluoromethylations with $PhTl(CF_3)_2$. Reaction of $TlPh(CF_3)_2$ with Hg in Glyme. Excess Hg, ca. 300 mg, and $TlPh(CF_3)_2$, 20 mg, were placed into a 4-mm Pyrex reactor, which was attached to the vacuum line and evacuated. After glyme, ca. 1 mL, was transferred into the reactor, the vessel was sealed and placed into an oil bath that was maintained at 65–68 °C for 4 days.

After 96 h, the fluorine NMR spectrum of the clear solution indicated the presence of $Hg(CF_3)_2$ (δ = 39.6 ppm; $^2J_{Hg-F}$ = 1304 Hz (lit.:[14] δ = 39.7 ppm; $^2J_{Hg-F}$ = 1294 Hz)) along with $PhTl(CF_3)_2$, as essentially the only fluorine-containing compounds in solution. Aside from very minor resonances (ca. 1%) arising from other thallium-containing species and a trace of CF_3H, the only other resonance observed (ca. 3%) was at 38.8 ppm. Based upon the relative intensities of the resonances, 3.55:1.00, the conversion of the thallium compound to $Hg(CF_3)_2$ was 78% complete under these conditions.

At the conclusion of the experiment, the presence of $Hg(CF_3)_2$ among the products was confirmed by mass spectrometry. A very small set of molecular ions corresponding to $HgPhCF_3$ was also observed.

Reaction of $TlPh(CF_3)_2$ with Hg in CH_2Cl_2. Methylene chloride, $TlPh(CF_3)_2$ (0.020 g), and Hg (0.200 g) were introduced into a reactor as above, and after the reactor was sealed, the contents were maintained at 65–70 °C. After 24 h, the fluorine NMR spectrum contained two new resonances (δ = 38.2 ppm, $^2J_{Hg-F}$ = 1004 Hz; δ = 39.2 ppm, $^2J_{Hg-F}$ = 1281 Hz) along with those of $TlPh(CF_3)_2$ (δ = 44.15 ppm; (J = 2069 Hz). The products, $HgPh(CF_3)$ (lit.: δ = 38.2 ppm; $^2J_{Hg-F}$ = 1008 Hz)[15] and $Hg(CF_3)_2$, were then present in the molar ratio 6.31:1.00. After 7 days the resonances of $Hg(CF_3)_2$ and $HgPhCF_3$ were equally intense, and a second Tl-containing compound (δ = 44.25 ppm; J = 2031 Hz) was also apparent.

After 17 days, however, the most intense peak in the ^{19}F NMR spectrum was from $Hg(CF_3)_2$, the molar ratio $Hg(CF_3)_2$:$HgPh(CF_3)$:$TlPh(CF_3)_2$ being 1.71:1.06:1.00. No resonances other than the four described above were present.

Overall, ^{19}F NMR spectroscopy indicated that after 17 days 66% of $TlPh(CF_3)_2$ was converted to either $HgPhCF_3$ or $Hg(CF_3)_2$. At the conclusion of the experiment, the presence of both $HgPh(CF_3)$ and $Hg(CF_3)_2$ was confirmed by mass spectrometry. In addition, an ion envelope centered at *m*/*e* 407, i.e., corresponding to $TlHg^+$, was evident in the spectrum.

Reaction of $TlPh(CF_3)_2$ wth $RhCl(PPh_3)_3$. After $TlPh(CF_3)_2$, 0.010 g (0.024 mmol), and $RhCl(PPh_3)_3$, 0.025 g (0.027 mmol), had been placed into a 4-mm reactor, CH_2Cl_2, ca. 0.5 mL, was added, and the ambient-temperature reaction was followed by ^{19}F NMR spectroscopy for 30 days. The major resonance observed was that due to the reagent, $TlPh(CF_3)_2$ (δ = 43.7 ppm; 100%), present with much less intense absorptions at 95 ppm (1.6%), 73.7 ppm (doublet of triplets; $^2J_{Rh-F}$ = 12 Hz; $^3J_{P-F}$ = 18 Hz; 0.4%), 27.4 ppm ($^2J_{Tl-F}$ = 5170 Hz; 2.6%), and –0.5 ppm (9%). The peak near 74 ppm was no longer observed after the reaction mixture was heated to 75 °C for 24 h.

Reaction of $Tl(CF_3)_2OAc$ with $Pd(PPh_3)_4$. In a 10-mL reactor 0.100 g (0.262 mmol) of $Tl(OAc)_3$ and 0.258 g (0.736 mmol) of $Cd(CF_3)_2$·glyme were stirred in 3 mL of CH_2Cl_2 for 40 min at room temperature, and then the supernatant was transferred to a second reactor that contained 0.100 g (0.086 mmol) of $Pd(PPh_3)_4$. The resulting solution was stirred at ambient temperature for 15 min and filtered; the volatile material was removed, yielding 0.015 g of a mixture, the ^{19}F NMR spectrum containing a triplet at 60.2 ppm ($^3J_{P-F}$ = 22 Hz), along with a second-order resonance at 59.0 ppm. The second complex is much more air sensitive than $Pd(CF_3)_2(PPh_3)_2$ and can be removed by exposure to the atmosphere. The isolated yield of $Pd(CF_3)_2(PPh_3)_2$[16] was 5%.

Results and Discussion

Synthesis of Bis(trifluoromethyl)phenylthallium. The overall diversity of the coordination chemistry of thallium has been widely discussed.[17] Briefly stated, in appropriately donating solvents organothallium compounds readily form mono- and dicoordinate adducts that are thought to contain ligands in tetrahedral and trigonal-bipyramidal arrays, respectively. In addition to these

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covalently bonded species, ionic compounds like TlR_2^+ and TlR^{2+} are also commonly encountered. The exceptionally stable ion $Tl(CH_3)_2^+$, for example, is soluble in and stable toward water, a property that is usually rationalized by comparison to the similarly substituted isoelectronic derivatives of the adjacent elements, $Hg(CH_3)_2$ and $Pb(CH_3)_2^{2+}$. Thus, one of the distinguishing aspects of organothallium chemistry is that numerous discrete products are often formed from even the most seemingly innocuous reaction.

One of the first findings of this preliminary study was that, at least with respect to the formation of numerous products from a seemingly straightforward reaction, the fluoroalkyl chemistry of thallium appears to be similar to the hydroalkyl chemistry. The complexity of the system was clearly demonstrated when the course of the trifluoromethylation of $TlPhCl_2$ with $Cd(CF_3)_2$·glyme was followed by fluorine NMR spectroscopy. Six different $TlCF_3$ compounds (which are readily distinguishable by their couplings to the thallium isotopes) were observed.[18] After 72 h, however, only two fluorine-containing compounds, the excess $Cd(CF_3)_2$·glyme and $TlPh(CF_3)_2$, are present in solution in significant amounts (see Figure 1). Note that the couplings of the thallium-203 and -205 isotopes to fluorine are not discrete in this spectrum. Ultimately, $TlPh(CF_3)_2$ is easily isolated in 87% yield.

The properties of the compound are all in accord with those expected. The mass spectrum, for example, contains only ions that can be attributed to the compound as formulated. When pure, $TlPh(CF_3)_2$ is thermally stable at ambient temperature and can be handled in the atmosphere, although it will slowly react as discussed below. Bis(trifluoromethyl)phenylthallium is initially soluble in relatively nonpolar solvents like CH_2Cl_2 or $CHCl_3$, but eventually it precipitates from solution as materials that cannot be redissolved into these solvents.

Attempted substitutions of acetate by CF_3 ligands had not been previously examined.[19] The results obtained here indicate that the reaction of $TlPh(OAc)_2$ with $Cd(CF_3)_2$·glyme proceeds much more rapidly than the reaction of $TlPhCl_2$, requiring only hours instead of days to proceed to completion, but there is a significant disadvantage to the employment of acetates as substrates. The reagent also reacts with acetate, resulting in the formation of CH_3COF; thus, much more $Cd(CF_3)_2$·glyme is required per mole of CF_3 in the product. When $Cd(CF_3)_2$·glyme and $TlPh(OAc)_2$ were present in a 1.3:1.0 mole ratio (a ratio commonly employed for the disubstitution of halides), the resulting yield of $TlPh(CF_3)_2$ was only 44%, based upon the amount of Tl taken. The precise stoichiometry of the acetate to acetyl fluoride transformation is still under study, but even based upon the reaction shown in eq 1, the yield of $TlPh(CF_3)_2$, 73%, is lower than those routinely obtained from the chloride. Under the conditions reported here, the amount of CF_3H produced from this reaction is very small.

$$TlPh(OAc)_2 + 2Cd(CF_3)_2\text{·glyme} \rightarrow TlPh(CF_3)_2 + 2CH_3COF \quad (1)$$

Proton and fluorine NMR studies have demonstrated that, in organothallium compounds, the coupling of these nuclei to thallium is dominated by the Fermi contact mechanism, by which, other things being equal, the magnitude of the coupling to Tl is expected to be related to the amount of s character in the carbon–thallium bond. For example, the Tl–H couplings in both of the series $Tl(CH_3)_nX_{3-n}$ and $Th(C_6F_5)_nX_{3-n}$, where X is halide, increase in the approximate ratio 1.0:1.7:4.0 as *n* decreases from 3 to 1.[20] Thus, the decrease in the observed Tl–H coupling, from 112 to 56 Hz for the para protons of the phenyl group upon trifluoromethylation of $TlPhCl_2$, reflects a decrease in the amount of s character in the Tl–Ph bond, perhaps indicative of a more polar Tl–arene bond in the product than in the reagent.

After exposure of $TlPh(CF_3)_2$ to the atmosphere for 2 days, three new fluorine-containing resonances are observed, CF_3H and two thallium-containing trifluoromethyl compounds (see Figure 3). Upon hydrolysis, $TlPh(CF_3)_2$ would be expected to give rise to three fluorine-containing products, as shown in eq 2 and 3.

$$TlPh(CF_3)_2 + H_2O \rightarrow Tl(CF_3)_2OH + PhH \quad (2)$$

$$TlPh(CF_3)_2 + H_2O \rightarrow TlPh(CF_3)OH + CF_3H \quad (3)$$

On the basis of the magnitude of the coupling constants, the resonances with the ^{205}Tl–F coupling constant of 3008 Hz are assigned to the strong base $Tl(CF_3)_2^+OH^-$. The second set, with the coupling constant of 3920 Hz, is assigned to $TlPh(CF_3)OH$. Resonances appearing only after 4 days (J = 5220 Hz) are thought to arise from (trifluoromethyl)thallium dihydroxide.[17,18,20]

Synthesis of (Trifluoromethyl)thallium Acetate. In several other systems the reactions of $Cd(CF_3)_2$·glyme have resulted in the complete substitution of halide ligands by trifluoromethyl groups.[19] After the determination that thallium acetate reacts with $Cd(CF_3)_2$·glyme much more rapidly than the chloride, one of the initial objectives of the $Tl(OAc)_3$ study was to determine if $Tl(CF_3)_3$ might be readily afforded by reaction with the cadmium reagent. The product isolated, however, was the disubstituted derivative, $Tl(CF_3)_2OAc$. The reaction of $Tl(CH_3)_2I$ with $Cd(CF_3)_2$·glyme was similarly designed to determine whether a trialkylthallane would be generated. No evidence for $Tl(CH_3)_2(CF_3)$ was obtained.

These results were not entirely unanticipated, since thallium(III) compounds are typically quite difficult to completely alkylate. For example, dialkylated compounds like $Tl(CH_3)_2Cl$ and $Tl(C_6F_5)_2Br$ are afforded by the actions of the appropriate Grignard reagent,[21] but complete substitution usually requires more powerful alkylating agents, e.g., lithium alkyls.[22] The difficulties associated with the formation of the third Tl–C bond appear to be a reflection of the extreme weakness of the bond, since pyrolytic studies of $Tl(CH_3)_3$ have led to an estimated bond dissociation energy of only 27.4 kcal/mol for the process $Tl(CH_3)_3 \rightarrow {}^{\bullet}Tl(CH_3)_2 + {}^{\bullet}CH_3$.[23]

Oxidative Trifluoromethylation Reactions. The purpose of this portion of the study was to investigate two somewhat interrelated questions. First, we wished to determine whether, under the types of conditions employed here, the low-energy reaction channel of, e.g., $TlPh(CF_3)_2$ would be reduction to Tl(I) or if some other process, such as the formation of thallium fluorides and CF_2, might be more favorable. Second, we wished to ascertain whether or not the addition of the ligands to a second center was reasonably efficient or if some other process like ligand coupling might predominate. In part, the substrates were chosen because of the range of the thermal stabilities of the metals in their higher oxidation states. Mercurials are known to be extremely robust whereas the triphenylphosphine derivatives of Rh(III) and Pd(II) are much more thermally fragile.

Reaction between $TlPh(CF_3)_2$ and Mercury. Although slightly elevated temperatures, 65 °C, are required, the oxidation of mercury proceeds smoothly in glyme, ultimately resulting in the

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(18) The (trifluoromethyl)thallium compounds that were initially present in largest amounts during the trifluoromethylation reactions that were carried out in noncoordinating solvents are characterized by Tl–F couplings of ca. 3800 and 5300 Hz. These resonances are assigned to covalent, e.g., $Tl(CF_3)X_2$, and ionic, e.g., $Tl(CF_3)X^+ + X^-$, forms of compounds containing one covalently linked Tl–CF_3 bond, respectively (see ref 17 and 20). Later in the course of the reaction, the amounts of (trifluoromethyl)thallium compounds with J_{Tl-F} coupling constants of ca. 2070 and 2980 Hz increase dramatically, the former eventually dominating the spectrum (see Figure 1). The first type of resonance arises from the title compound, e.g., $Tl(CF_3)_2OAc$. The second is currently attributed to an ionic species $Tl(CF_3)_2^+$, e.g., $Tl(CF_3)_2^+ + OAc^-$, which, of course, is isoelectronic with the very stable mercurial $Hg(CF_3)_2$ and is analogous to the well-known, and very stable, $Tl(CH_3)_2^+$.

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formation of $Hg(CF_3)_2$ in very good yield, 80%, as judged by NMR spectroscopy. Both the mass spectrum and the NMR data are in accord with the presence of trace amounts of $HgPh(CF_3)$ among the products. The conditions required for the oxidative trifluoromethylation of elemental mercury are milder than those previously reported for the analogous reaction of $Tl(C_6F_5)_2Br$ with Hg, which required 7 days at 130 °C.[24]

In the less polar solvent CH_2Cl_2 the reaction proceeds much more slowly than in glyme, and it was possible to examine the course of the reaction in a more detailed fashion. The results suggest that the steps of the trifluoromethylation are as shown in eq 4–6.

$$TlPh(CF_3)_2 + Hg \rightarrow PhHgTl(CF_3)_2 \qquad (4)$$

$$PhHgTl(CF_3)_2 \rightarrow HgPh(CF_3) + Tl(CF_3) \qquad (5)$$

$$Tl(CF_3) + HgPh(CF_3) \rightarrow Hg(CF_3)_2 + TlPh \qquad (6)$$

The initial step of the proposed reaction sequence consists of the insertion of mercury into the relatively ionic TlPh bond. The intermediate bimetallic species formed appears to be more stable in CH_2Cl_2 than in the more polar glyme. Attempts to demonstrate the presence of the intermediate by mass spectrometry were unsuccessful, although ions corresponding to $TlHg^+$ were easily observed.

The second step of the reaction scheme, reductive elimination from $PhHgTl(CF_3)_2$, generates $HgPh(CF_3)$, the mercurial experimentally observed to be present in highest concentration during the initial stages of the reactions carried out in CH_2Cl_2. The final step, ligand exchange between $Tl(CF_3)$ and $HgPh(CF_3)$, which is rapid in glyme but relatively slow in CH_2Cl_2, leads to $Hg(CF_3)_2$, the product that is eventually found in highest concentration in either solvent.

The mechanism proposed by eq 4–6 predicts that both the bimetallic species $PhHgTl(CF_3)_2$ and the monovalent $Tl(CF_3)$ possess reasonable thermal stability in CH_2Cl_2. Additionally, eq 6 predicts that $Tl(CF_3)$, once isolated, will be a stronger trifluoromethyl ligand exchange reagent than $Hg(CF_3)_2$. Experiments designed to test these hypotheses are currently in progress, but we note that the lower valent gold(I) compound $Au(CF_3)PMe_3$ has been shown to be a very effective trifluoromethylating agent, superior to $Cd(CF_3)_2$·glyme in some cases.[16]

Reaction of $RhCl(PPh_3)_3$ with $TlPh(CF_3)_2$. At ambient temperature the reaction of $RhCl(PPh_3)_3$ with $TlPh(CF_3)_2$ proceeds to a slight extent, generating a compound whose ^{19}F couplings (J_{Rh-F} = 12 Hz; J_{P-F} = 18 Hz) and chemical shift (δ = 73.7 ppm) are sufficiently similar to those reported for $Rh(CF_3)Cl_2(CO)(PMe_2Ph)_2$ (J_{Rh-F} = 14 Hz; J_{P-F} = 18 Hz; $\delta(^{19}F)$ = 75.3 ppm)[25] to strongly suggest the formation of a rhodium(III) trifluoromethyl complex. Even after 30 days, however, the amount of this compound present was much too small to separate and it decomposed upon heating. This finding is in contrast to the results obtained when $Tl(C_6F_5)_2Br$ and $RhCl(PPh_3)_3$ were allowed to interact, resulting in the formation of $RhCl(C_6F_5)_2(PPh_3)_2$, in an unspecified yield.[26]

Reaction of $Pd(PPh_3)_4$ with $TlPh(CF_3)_2OAc$. Of the metallic species described here, only the palladium complex, $Pd(PPh_3)_4$, is smoothly oxidized at ambient temperature. The expected product, $Pd(CF_3)_2(PPh_3)_2$, can be isolated, but only in very small amounts.

Summary

To summarize, $TlPh(CF_3)_2$ and $Tl(CF_3)_2OAc$ are easily prepared in CH_2Cl_2 by the action of $Cd(CF_3)_2$·glyme upon appropriate substrates. Of the species soluble in CH_2Cl_2, the bis(trifluoromethyl)thallium compounds are the least reactive with air, which forms the basis of very convenient separation procedures.

Oxidative trifluoromethylation reactions with mercury proceed readily at slightly elevated temperatures to form first $HgPh(CF_3)$ and then $Hg(CF_3)_2$. Attempted oxidations of $RhCl(PPh_3)_3$ and $Pd(PPh_3)_4$ were less successful, since the former was insufficiently reactive whereas the reaction with the Pd^0 complex led to a variety of products.

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Registry No. $TlCl_3$, 13453-32-2; $BPh(OH)_2$, 98-80-6; $TlPhCl_2$, 19628-33-2; AgOAc, 563-63-3; $TlPh(OAc)_2$, 20425-82-5; TlI, 7790-30-9; $TlMe_2I$, 7066-67-3; $Cd(CF_3)_2$·glyme, 76256-47-8; $TlPh(CF_3)_2$, 121029-71-8; $Tl(OAc)_3$, 2570-63-0; $Tl(CF_3)_2OAc$, 121029-72-9; $Hg(CF_3)_2$, 371-76-6; $HgPhCF_3$, 24925-18-6; $RhCl(PPh_3)_3$, 14694-95-2; $Pd(PPh_3)_4$, 14221-01-3; $Pd(CF_3)_2(PPh_3)_2$, 114237-06-8.

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