

Synthesis of New Cadmium Alkyls by Cocondensation of Cadmium Vapour with Trifluorosilyl and Trifluoromethyl Radicals

M. A. Guerra, T. R. Bierschenk, and R. J. Lagow*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

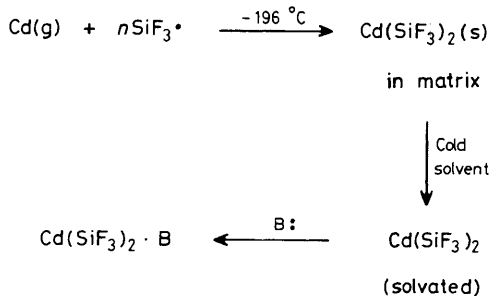
The very reactive new compounds $\text{Cd}(\text{SiF}_3)_2$ and $\text{Cd}(\text{CF}_3)_2$ have been prepared by cocondensation of cadmium vapour with trifluorosilyl and trifluoromethyl radicals, ^{19}F n.m.r. spectroscopy showing that $\text{Cd}(\text{SiF}_3)_2$ slowly decomposes at room temperature while $\text{Cd}(\text{CF}_3)_2$ decomposes at $+5^\circ\text{C}$; the addition of glyme (1,2-dimethoxyethane) at low temperature allowed $\text{Cd}(\text{SiF}_3)_2 \cdot \text{glyme}$ and $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}$ to be isolated at room temperature.

Currently there is interest in base-stabilized trifluoromethyl compounds of cadmium for use as alkylation agents.¹⁻⁴ While such base-stabilized complexes have been known for some time,¹⁻⁵ ligand-free (homoleptic) trifluoromethyl cadmium compounds have eluded synthesis owing to their thermal instability. Further, no trifluorosilyl compounds of cadmium are known.

The synthesis of alkyls by the cocondensation of metal atoms with an excess of alkyl radicals has enabled new compounds of marginal stability to be synthesized.⁶ The compounds $\text{Cd}(\text{CF}_3)_2$ and $\text{Cd}(\text{SiF}_3)_2$ are much more reactive than their base-stabilized relatives and are reactive intermediates for reactions with other reagents and bases.

We have generated trifluoromethyl and trifluorosilyl radicals using a low-energy (10 MHz, 80 W) radio-frequency source from hexafluoroethane and hexafluorodisilane precursors⁶ and cocondensed them with Cd in excess onto a rotating thin-walled stainless-steel cold-finger reactor⁷ (-196°C) (see Scheme 1 for SiF_3 example).

After a 2 h reaction, the excess of Si_2F_6 was removed *in vacuo* at -78°C . Extraction with methylene chloride at -78°C gave bis(trifluorosilyl)cadmium. The low temperature ^{19}F n.m.r. spectrum of the product, $\text{Cd}(\text{SiF}_3)_2$, as a solvated species in methylene chloride, was determined (Table 1). The ^{19}F n.m.r. data showed that decomposition began at *ca.* 20°C , and *ca.* one-third of the compound had decomposed after 16 h



Scheme 1. B: = glyme or other two-electron donor.

at 25 °C. The mass spectrum of $\text{Cd}(\text{SiF}_3)_2$ gave the expected isotope pattern for each cadmium fragment: $\text{Cd}(\text{SiF}_3)_2^+$ (1.4%), $\text{Cd}(\text{SiF}_3)\text{SiF}_2^+$ (2%), CdSiF_3^+ (75%), Cd^+ (58%), and SiF_3^+ (100%). I.r. absorptions occurred at 1250m, 1070br. s, 1005s, and 785m cm^{-1} .

$\text{Cd}(\text{SiF}_3)_2$ can be co-ordinated by glyme and recrystallization from hexane gave the white adduct $\text{Cd}(\text{SiF}_3)_2 \cdot \text{glyme}$ (10.9%), m.p. 88–90 °C. The ^1H n.m.r. data are in Table 1. The mass spectrum gave the expected isotope pattern for each cadmium fragment: CdSiF_3^+ (9%), $\text{Cd} \cdot \text{glyme}^+$ (1%), Cd^+ (15%), glyme^+ (8%), and SiF_3^+ (100%). I.r. absorptions occurred at 2920br. m, 1400m, 1250m, 1120w, 1070br. s, 1005s, and 785m cm^{-1} .

Similarly, the cocondensation of Cd vapour with an excess of CF_3 radicals was carried out for 3 h. Excess of C_2F_6 was removed *in vacuo* at –131 °C. The $\text{Cd}(\text{CF}_3)_2$ produced was unstable at room temperature, its low-temperature ^{19}F n.m.r. spectrum showing that it decomposes in solution at 5 °C. Addition of glyme at –78 °C, extraction with Et_2O , and recrystallisation from hexane gave $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}$ (9%) (see Table 1 for ^1H n.m.r. data). Its mass spectrum showed $\text{CdCF}_3 \cdot \text{glyme}^+$ as the highest mass fragment, together with the fragment ions Cd^+ and FCdCF_3^+ . The n.m.r. and mass spectral data are in good agreement with those found in the literature.

Morrison and co-workers have shown^{1–4} that under mild conditions $(\text{CF}_3)_2\text{Cd} \cdot \text{glyme}$ and $(\text{CF}_3)_2\text{Cd} \cdot \text{pyridine}$ are

Table 1. ^{19}F and ^1H N.m.r. data for SiF_3 and CF_3 cadmium complexes.^a

| Compound | ^{19}F , $\text{Cd}(\text{XF}_3)_2$ | | ^1H , glyme | |
|--|--|--------------------|----------------------|-----|
| | XF_3 | $J(\text{Cd-F})^c$ | CH_2 | Me |
| $\text{Cd}(\text{SiF}_3)_2$ | 102.3 | 601/564 | — | — |
| $\text{Cd}(\text{SiF}_3)_2 \cdot \text{glyme}^b$ | 98.7 | 581/556 | 3.7 | 3.5 |
| $\text{Cd}(\text{CF}_3)_2$ | 38.5 | 543/508 | — | — |
| $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}^b$ | 33.2 | 492/460 | 3.6 | 3.4 |

^a Spectra were recorded for dilute solutions in CD_2Cl_2 at –80 °C for the free compounds and at room temperature for the glyme complexes, with external SiMe_4 and CFCl_3 as standards for ^1H and ^{19}F , respectively. Shifts are in p.p.m. and coupling constants in Hz. ^b glyme = $(\text{MeOCH}_2)_2$. ^c $^{113}\text{Cd}/^{111}\text{Cd}$.

powerful fluoroalkylating agents and low-temperature sources of difluorocarbene. They have synthesized several main-group and transition-metal trifluoromethyl compounds and found that these cadmium complexes are much more active than $(\text{CF}_3)_2\text{Hg}$ as alkylating agents. The $\text{Cd}(\text{SiF}_3)_2$ compounds are of interest as trifluorosilylation agents and as sources of difluorosilylene in solution.

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