A New Trifluorosilyl Exchange Reagent: Reactions of $Cd(SiF_3)_2$·glyme (glyme = dimethoxyethane) with Dibromo Metal Phosphine Complexes of Platinum, Palladium, and Nickel yield Trifluorosilyl Substituted Dialkyl Compounds

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The reaction of excess $Cd(SiF_3)_2$·glyme (glyme = dimethoxyethane) with trimethylphosphine metal dibromides of platinum, palladium, and nickel yielded the trifluorosilyl substituted dialkyl compounds *trans*-$Pt(SiF_3)_2(PMe_3)_2$, $Pd(SiF_3)_2(PMe_3)_2$, and $Ni(SiF_3)_2(PMe_3)_3$.

Although a general synthesis of trifluorosilyl metal analogues has recently been developed through the reactions of metal vapours,[1] there are still many unknown compounds in the trifluorosilyl metal class and a conventional synthetic method is an important addition to the homoleptic synthetic capabilities in the area.[2] Of course metal alkyls are most often formed by reaction of metal halides and an appropriate alkylating agent, primarily an alkyl-lithium compound, a Grignard reagent, or an aluminum alkyl. The instability (decomposes > −78 °C), and therefore lack, of this type of trifluorosilyl

Table 1. Yields and properties of $M(SiF_3)_2(PMe_3)_x$ (M = Ni, Pd, Pt).[a]

Initial compounds	Amount reacted /mg	Isolated compounds	Yields /mg (%)
$NiBr_2(PMe_3)_3$	200	$Ni(SiF_3)_2(PMe_3)_3$	31 (15)
$PdBr_2(PMe_3)_2$	200	$Pd(SiF_3)_2(PMe_3)_2$	33 (16)
$PtBr_2(PMe_3)_2$	200	$Pt(SiF_3)_2(PMe_3)_2$	41 (20)

[a] High resolution mass spectra confirmed each molecular ion with an error of 2, 2, and 1 p.p.m., respectively. Melting points: 160 (decomp.), 186—188, and 197 °C, respectively.

Table 2. ^{19}F NMR and ^{1}H NMR spectral data of trifluorosilyl metal trimethylphosphine compounds.[a]

Compound	SiF_3[b]	J(P–F)[c]	J(M–F)[c,d]	Me[b]
$Ni(SiF_3)_2(PMe_3)_3$	89.4 q	5.9	—	1.40
$Pd(SiF_3)_2(PMe_3)_2$	96.9	—	—	1.10
$Pt(SiF_3)_2(PMe_3)_2$	87.8 t	7.8	269.7	1.86

[a] ^{19}F NMR and ^{1}H NMR spectra were recorded in a dilute solution of CD_2Cl_2 and referenced to external $CFCl_3$ and tetramethylsilane (TMS), respectively. [b] Chemical shifts given in p.p.m. [c] Coupling constants given in Hz. [d] ^{197}Pt.

analogue to an alkylation reagent has limited significantly the number of known metal trifluorosilyl compounds.

Previously reactions of trifluoroiodosilane with dimeric carbonyls of cobalt, manganese, and rhenium have led to singly substituted trifluorosilyl compounds and metal carbonyl iodides.[3]

Bis(trifluorosilyl)mercury[2] may also be used as a trifluorosilylation reagent although the mercury–silicon bond is so much stronger that forcing conditions would be required to allow an exchange reaction to occur in certain metal halide systems. Forcing conditions are often incompatible with the basic stability problems associated with reactions designed to produce the unknown and co-ordinatively unstable metal trifluorosilyl compounds.

After bis(trifluorosilyl)cadmium was first prepared in our laboratory, we had reason to suspect that the compound might be an excellent trifluorosilylation reagent. Recently Morrison and co-workers[4] have established that the trifluoromethyl alkyl analogue has many advantages as a trifluoromethyl transfer reagent over earlier work with bis(trifluoromethyl)-mercury.[5]

The first synthesis of bis(trifluorosilyl)cadmium·glyme (glyme = dimethoxyethane) was accomplished by the reaction of trifluorosilyl radicals with cadmium vapour.[6] Bis(trifluorosilyl)cadmium·glyme was prepared by the addition of glyme to bis(trifluorosilyl)cadmium.

Such exchange reactions occur when a slight excess of $Cd(SiF_3)_2$·glyme is reacted with 200 mg of the dibromo metal phosphine compounds in ether at 25 °C. After stirring for one hour, the solution is extracted and the nonvolatiles are sublimed to give the bis(trifluorosilyl)metal compounds. The yields and properties of the trifluorosilyl analogues are listed in Table 1. The ^{19}F NMR and ^{1}H NMR spectroscopic data are summarized in Table 2.

$Pd(SiF_3)_2(PMe_3)_2$ and $Ni(SiF_3)_2(PMe_3)_3$ were previously prepared by the reaction of trifluorosilyl radicals with metal vapours.[1] These compounds were characterized by comparison with previously prepared compounds of the same identity. The first new compound prepared using the trifluorosilyl cadmium reagent is *trans*-$Pt(SiF_3)_2(PMe_3)_2$. The ease of ligand exchange with $Cd(SiF_3)_2$·glyme and dibromo metal phosphine complexes parallels the observations of Morrison for $Cd(CF_3)_2$·glyme[4] and suggests that this reagent can be used for ligand exchange with main group metal halides, Lewis base exchange, and even in organic related syntheses in the future.

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