Trifluoromethyl Group 2B Compounds: Formation of Mono- and Bis-(trifluoromethyl)–Platinum, –Palladium, and –Nickel Trialkylphosphine Complexes from the Reaction of $(CF_3)_2Cd{\cdot}glyme$ [glyme = $(CH_2OMe)_2$] with the Diligand Metal Dihalides

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Summary The reaction of $(CF_3)_2Cd{\cdot}glyme$ [glyme = $(CH_2OMe)_2$] with bis(trialkylphosphine) Group 8B dihalides like $Br_2Ni(PEt_3)_2$ during short periods of time, 0·5—5 h, results in the formation of the monosubstituted compounds $(CF_3)BrNi(PEt_3)_2$, $(CF_3)BrPd(PEt_3)_2$, and $(CF_3)IPt(PBu^n_3)_2$ in 60—70% yield; over longer periods of time, in the presence of an excess of $(CF_3)_2Cd{\cdot}glyme$, the disubstituted compounds, $(CF_3)_2M(PEt_3)_2$ (M = Ni, Pd, and Pt) are formed.

Organometallic compounds that contain σ-bonded perhydrogenated alkyl ligands are most often formed by the reaction between a halide of the desired metallic species and an appropriate alkylating agent, *e.g.*, LiMe, MeMgX, or $PbMe_4$, the latter chosen from a well known series of reagents that possesses a wide range of reactivity. Although, in principle, an analogous series of ligand exchange reagents for the formation of perfluoroalkyl organometallic compounds could exist, in fact, no such series is presently known. Thus the preparation of many perfluorinated organometallic compounds is difficult since the currently available syntheses frequently require equipment and techniques, *e.g.*, metal atom reactors or discharge apparatus, which are often not readily available.[1]

While little explored, ligand exchange reactions between trifluoromethyl Group 2B compounds and inorganic substrates constitute, potentially, a very attractive method for forming perfluoroalkyl-substituted organometallic species. Recently, we isolated the (trifluoromethyl)cadmium compound, $(CF_3)_2Cd{\cdot}glyme$ (glyme = $MeOCH_2CH_2OMe$) and examined three representative types of reaction of this species: Lewis base exchange, ligand exchange with main group halides, and the reaction with acyl halides.[2] The present communication presents the reactions of $(CF_3)_2Cd{\cdot}glyme$ with a fourth major class of reagent: low valent, late transition metal complexes; the divalent bis(trialkylphosphine) dihalides of the nickel triad were selected as representative of this type of compound.

To prepare the monosubstituted derivatives, $(CF_3)XM(PR_3)_2$, equimolar amounts, 1—2 g, of $(CF_3)_2Cd{\cdot}glyme$[2] and the diligand metal dihalide are introduced into a flask along with 20 ml of solvent, CH_2Cl_2 or diethyl ether. After the ambient temperature reaction, see Table 1, the material in the flask is removed from the glove box and the products are recovered; recrystallization from light petroleum or hexane in air yields the expected $(CF_3)XM(PR_3)_2$, M = Ni, Pd, or Pt compound in 60—70% yield. Reagents, reaction times, and product characterization are found in Table 1.

Table 1. Preparation of $(CF_3)XM(PR_3)_2$,[a] M = Pt, Pd, Ni.

Reagent	Time/h	% Yield	δ, ^{19}F [b] ($^3J_{P-F}$/Hz)
$I_2Pt(PBu^n_3)_2$	5	60	−69·6 (19)
$Br_2Pd(PEt_3)_2$	0·5	70	−69·6 (32)
$Br_2Ni(PEt_3)_2$	0·5	65	−70·2 (22)

[a] In each case mass spectrometry indicated strong molecular ions, *M*, as well as [*M* − X] and [*M* − CF_3] ions; the errors in the experimental exact mass determinations of the molecular ions were: 10, 7, and 0 p.p.m., respectively. Melting points: 67—69, 99 [lit. (ref. 3) 96—97], and 56—58 °C, respectively. [b] In p.p.m.: positive chemical shifts shielded *vs.* ext. trifluoroacetic acid.

Except for the relative ratios of reagents and the times involved, Table 2, the procedures used for the formation of the disubstituted compounds, $(CF_3)_2M(PEt_3)_2$, M = Pt, Pd, or Ni, are very similar to those for the monosubstituted compounds, above. The solvent was diethyl ether; recrystallization was from light petroleum.

Table 2. Preparation of $(CF_3)_2M(PEt_3)_2$ [a] $M = Pt, Pd, Ni$.

Reagent	Mole ratio [b]	Time/ h	% yield	δ, ^{19}F [c] ($^3J_{P-F}$/Hz)
$I_2Pt(PEt_3)_2$	2 : 1	24	45	−63·9 (12)
$Br_2Pd(PEt_3)_2$	4·2 : 1	31	35	−61·1 (19)
$Br_2Ni(PEt_3)_2$	3·2 : 1	8	*ca.* 5	−64·3 (11)

[a] All properties fully in accord with the formulation of the species as indicated, *e.g.*, the mass spectra contain $[M - F]$ (*ca.* 15%) and $[M - CF_3]$ (100%) ions. Typical exact mass error (M − F ion): 10 p.p.m. [b] $(CF_3)_2Cd\cdot$glyme: $X_2M(PEt_3)_2$. [c] As in Table 1, footnote b.

Because of the reactivity of the trifluoromethylating agent, $(CF_3)_2Cd\cdot$glyme[2], the present procedure has several advantages over those previously reported.[1,4,5] The most obvious is that the reactions appear to proceed by simple ligand exchange allowing the use of metal reagents which are in their common oxidation states. Although the reactions of only the divalent elements of the nickel triad are reported here, the exchange appears to be general since other low-valent metal complexes *e.g.*, dihalogenocobalt trialkylphosphines also form trifluoromethyl derivatives by the analogous reaction with $(CF_3)_2Cd\cdot$glyme.

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[5] Except for the metal atom reactions, previous syntheses of this type of compound have been almost entirely restricted to the oxidative-addition reactions of CF_3I or the reactions of CF_3COCl with metal carbonyls or carbonylate anions. The success of the latter reactions is of course, dependent upon the facile thermal decarbonylation of the acyl species. See P. M. Treichel and F. G. A. Stone, *Adv. Organomet. Chem.*, 1964, **1**, 143; H. J. Emeleus, 'The Chemistry of Fluorine and its Compounds,' Academic Press, New York, 1969.