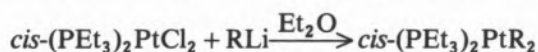
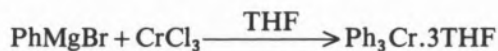




# ORGANOPENTAFLUOROSILICATES: A REAGENT FOR THE SYNTHESIS OF $\sigma$ -BONDED ORGANOTRANSITION METAL COMPOUNDS

*A novel reaction between  $[\text{NH}_4]_2[\text{RSiF}_6]$  and  $\text{L}_2\text{MX}_2$ , where  $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$ ;  $\text{L} = \text{PPh}_3, \text{PPh}_2\text{CH}_2$ ;  $\text{M} = \text{Ni, Pt}$ , is described, providing a useful route to  $\sigma$ -bonded organonickel(II) and organoplatinum(II) derivatives.*

Organotransition metal compounds having one electron donor neutral ligands, such as methyl, phenyl etc. are of vast interest for their use in organic synthesis and of their relevance in biochemistry [1]. The normal route to these compounds is the treatment of a metal halide complex with excess Grignard reagent [2] or with organoalkalimetal derivatives [3] in ether solutions:



where  $\text{R} = \text{Me, Ph}$  etc.

Organolithium reagents are more reactive than Grignard reagents and more readily give fully alkylated products. There are also some complications in these reactions. Hence, various chemists have sought alternative routes to these compounds. Reagents like tetraethyllead [4], trialkylaluminium [5], dialkyl- or aryl-mercury [6] etc. have also been used for the alkylation and arylation but with limited success.

Recently EABORN and co-workers [7] have described a new route to alkyl-, aryl-platinum compounds by using organotin compounds.

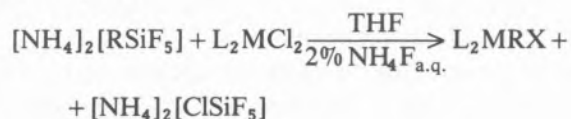
Organopentafluorosilicates are easily available and have been used as alkylating and arylating reagents for various main group metals and metalloids [8] very efficiently. This reagent was being neglected for a long time inspite of its usefulness. Recently, KUMADA and his co-workers [9] have initiated exploiting this novel reagent for the formation of carbon-halogen, carbon-oxygen and carbon-carbon bonds. Their success has opened a new era in the syntheses of various organic compounds. To ease the problem of low solubility of various organopentafluorosilicates in organic solvents, they have established solid state reactions of potassium-alkyl-, alkenyl-pentafluorosilicates for the formation of carbon-carbon bonds [10]. Keeping this development and vital importance of  $\sigma$ -carbontransition metal compounds in view, we planned to explore the use of organopentafluorosilicates to synthesize organotransition metal complexes.

Thermal instability of organotransition metal complexes ruled out the use of solid state reactions. Hence, we had to look for organopentafluorosilicates, which are fairly soluble in water and in water soluble ethers containing dilute aqueous solution

of an alkali metal fluoride. Our literature survey revealed that diammonium organopentafluorosilicates are the most suitable reagents for their maximum solubility in water.

In our preliminary attempts, we successfully reacted organopentafluorosilicates in THF solution, containing 2% aqueous ammonium fluoride solution, with transition metal halide complexes of the type  $L_2MX_2$  in THF solution at  $-10^\circ$  to  $0^\circ$  temperature. Instantaneous decolourization of the metal halide solution was observed, giving finally a pale yellow to colourless reaction mixture. Normal work up of the reaction mixture gave colourless to pale yellow coloured solids of the complexes  $L_2MRX$  and  $L_2MR_2$ , as desired, where L is a stabilizing ligand such as triphenylphosphine or 1,2-diphenylphosphinoethane, M is Ni(II) or Pt(II), R is methyl or phenyl and X is chlorine.

Methyl- and phenyl-pentafluorosilicates were easily prepared in very good yields as per literature method [11]. These were then reacted with  $(PPh_3)_2MCl_2$  or  $(PPh_2CH_2)_2MCl_2$  to give  $(PPh_3)_2MRX$ ,  $(PPh_3)_2MR_2$  and  $(PPh_2CH_2)_2MR_2$  in good yields:



where, R = Me, Ph; M = Ni, Pt; X = Cl or Me.

These compounds have been characterized by their physical properties, which are summarized in Table 1, and they are in good agreement with the literature values [12<sup>a-h</sup>].

This new method is especially attractive because the other product, the diammonium pentafluorosilicate, remain in aqueous solution and does not interfere with the isolation of the products, and is easily removable together with the unreacted organopentafluorosilicates. This method has also advantage over the conventional metathesis method because this new reagent gives no side reaction and gives substantial amounts of either  $L_2MRX$  or  $L_2MR_2$  complexes depending on the ratio of the reactants. Moreover work-up of the products from reactions involving Grignard or organolithium reagents usually involves a hydrolysis step to destroy any residual reagents, and this is known to give complications [12<sup>c</sup>]. Moreover, this reagents is less expensive and much more easily prepared than any other existing organometallic reagents for alkylation or arylation. This reagent is also much less toxic than the organometallic reagents such as organolead, organomercury, organotin, etc.

Our preliminary studies have, therefore, established that our method can potentially be developed as a general method to form  $\sigma$ -carbon-transition metal complexes in fairly good yields.

## EXPERIMENTAL

All the reactions were carried out in quickfit apparatus. Methyl- and phenyl-trichlorosilane were obtained from Hopkin and Williams.

## IR, AND NMR SPECTRA

IR spectra recorded by using a PERKIN-ELMER 580 spectrophotometer ( $4000-400\text{ cm}^{-1}$ ) in nujol

Table 1  
Physical constants (literature value given in brackets) of some  $L_2MR_2$  compounds prepared by the organopentafluorosilicate route

L	M	R	% yield	M.P. °C	$\delta$ M-R	NMR/ppm* $\delta$ P-Ph	$\delta$ P-CH <sub>2</sub> CH <sub>2</sub> -P
PPh <sub>2</sub>	Ni	Me	70	81	-1.00s	7.00m	
»	»	Me(Cl)	65	105	-0.80s	6.90m	
»	»	Ph	68	75	6.85m	7.20m	
»	Pt	Me	73	235-237(238-39) [12a]	0.35q(0.31q) [12b]	7.45m	
»	»	Me(Cl)	70	274(273-278) [12h]	0.00q	7.25m	
»	»	Ph	70	158-160(144-160) [12c]	6.90m	7.50m	
PPh <sub>2</sub> CH <sub>2</sub>	Ni	Me	65	130(130) [12d]	0.80d(0.80d) [12d]	7.40m	1.70t(1.80t) [12d]
»	»	Ph	70	95	6.90m	7.35m	1.75t
»	Pt	Me	80	220-225(220-223) [12e]	1.10d(1.8d) [12f]	7.38m	1.50m(1.42m) [12f]
»	»	Ph	75	210-214(207-212) [12g]	6.75m	7.38m	1.60t

\* values in ppm from TMS in C<sub>6</sub>D<sub>6</sub> solution, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet

mull. NMR spectra were recorded on a PERKIN-ELMER EM360 (60MHz) instrument using TMS as internal standard.

#### ANALYTICAL METHODS

Carbon, hydrogen were determined by microanalytical methods. Phosphorus, nickel, platinum and chlorine were determined by standard methods.

#### A) Diammoniummethyl (or phenyl) pentafluorosilicates:

Diammonium (methylpentafluorosilicate) and diammonium- (phenylpentafluorosilicate) were prepared, in good yields, as per literature method [11].

#### B) Metal halide complexes

Dichloro bis (triphenyl phosphine) nickel(II) [13], dichloro [1,2- bis (diphenyl phosphino) ethane] nickel(II) [14], dichloro bis (triphenyl phosphine) platinum(II) [15] and dichloro [1,2-bis (diphenyl phosphino) ethane] platinum(II) [16] were prepared as per standard literature methods.

#### C) $\sigma$ -Carbon-metal complexes:

##### i) Bis (triphenyl phosphine) dimethylnickel(II): $(PPh_3)_2NiMe_2$

To a solution of diammonium (methylpentafluorosilicate) (0.02 mole; 3.48 g) in THF (200 cm<sup>3</sup>) and 2% aq. ammonium fluoride solution (20 cm<sup>3</sup>), kept stirred at  $-10^\circ$ , was added a solution of dichloro bis (triphenyl phosphine) nickel(II) (0.01 mole; 7.43 g) in THF (100 cm<sup>3</sup>). The deep colour of the halide complex was discharged instantaneously, finally giving a pale coloured solution. The reaction mixture was treated with ice-water (30 cm<sup>3</sup>) at  $-10^\circ$  and was quickly extracted with  $3 \times 50$  cm<sup>3</sup> ether. The ether layer was washed with ice-water and stored over anhydrous sodium sulphate at  $-10^\circ$  for 24 h. After quick filtration, ether was stripped off under vacuum at  $0^\circ$ , leaving some solid residue. The residue was treated with cold pentane (10 cm<sup>3</sup>) and the solution was digested with methanol (10 cm<sup>3</sup>) and was stored at  $-20^\circ$ . Almost colourless crystals were formed which were filtered, dried under vacuum and stored at  $-20^\circ$  (70%), mp.  $81^\circ$  (dec.) (Found C, 74.20; H, 5.73; Ni, 9.42; P, 10.00;  $C_{38}H_{36}NiP_2$  requires: C, 74.41; H, 5.92; Ni, 9.57; P, 10.10%) IR (nujol)  $\nu$  (Ni-C) 1150 cm<sup>-1</sup>.

##### ii) Chloro (methyl) bis (triphenylphosphine) nickel(II): $(PPh_3)_2Ni(Cl)Me$

An identical reaction as in (i) with diammonium-methylpentafluorosilicate and dichloro bis (triphenyl phosphine) nickel(II) in 1:1 ratio gave the title product (65%), mp.  $105^\circ$  (dec.) (Found: C, 70.00; H, 5.21; Cl, 5.49; Ni, 9.21; P, 9.80;  $C_{37}H_{33}ClNiP_2$  requires: C, 70.12; H, 5.25; Cl, 5.59; Ni, 9.26; P, 9.78%) IR (nujol)  $\nu$  (Ni-C) 1155 cm<sup>-1</sup>.

##### iii) Bis (triphenyl phosphine) diphenylnickel(II): $(PPh_3)_2NiPh_2$

An identical reaction as in (i) with diammonium-(phenylpentafluorosilicate) and dichloro bis (triphenylphosphine) nickel(II) in 2:1 molar ratio gave the desired product (68%) mp.  $75^\circ$  (dec.) (Found: C, 78.00; H, 5.50; Ni, 7.80; P, 8.38;  $C_{48}H_{40}NiP_2$  requires: C, 78.18; H, 5.46; Ni, 7.96; P, 8.40%) IR (nujol)  $\nu$  (Ni-Ph) 1000 cm<sup>-1</sup>.

##### iv) [1,2-Bis (diphenyl phosphino) ethane] dimethylnickel(II): $(PPh_2CH_2)_2NiMe_2$

A similar reaction as in (i) between diammonium-(methylpentafluorosilicate) and [1,2-bis (diphenylphosphino) ethane] dichloronickel(II) in 2:1 molar ratio gave the desired product (65%) mp.  $130^\circ$  (dec.) (lit. [12d] mp.  $130^\circ$  dec.) (Found: C, 68.80; H, 6.10; Ni, 11.98; P, 12.60;  $C_{28}H_{30}NiP_2$  requires: C, 69.02; H, 6.21; Ni, 12.05; P, 12.72%) IR (nujol)  $\nu$  (Ni-Me) 1080 cm<sup>-1</sup>.

##### v) [1,2-Bis (diphenyl phosphino) ethane] diphenylnickel(II): $(PPh_2CH_2)_2NiPh_2$

An identical reaction as in (i) between dichloro-[1,2-bis (diphenyl phosphino) ethane] nickel(II) and diammonium (phenylpentafluorosilicate) in 1:2 molar ratio gave the title compound (70%) mp.  $95^\circ$  (dec.) (Found: C, 74.48; H, 5.28; Ni, 9.60; P, 10.16;  $C_{38}H_{34}NiP_2$  requires: C, 74.66; H, 5.60; Ni, 9.60; P, 10.04%) IR (nujol)  $\nu$  (Ni-Ph) 1080 cm<sup>-1</sup>.

##### vi) Bis (triphenylphosphine) dimethylplatinum(II): $(PPh_3)_2PtMe_2$

To a solution of diammonium (methylpentafluorosilicate) (0.005 mole; 0.87 g) in THF (200 cm<sup>3</sup>) and 2% aq. ammonium fluoride solution (20 cm<sup>3</sup>) kept stirred at room temperature, was added a solution

of dichlorobis (triphenyl phosphine) platinum(II) (0.002 mole; 1.52 g) in THF (200 cm<sup>3</sup>). The resulting mixture was stirred at room temperature for 30 min. Usual work-up yielded the desired product (73 %) mp. 236° (dec.) (lit. [12<sup>a</sup>], mp. 238-39°) (Found: C, 60.60; H, 4.72; P, 8.20; Pt, 26.00; C<sub>38</sub>H<sub>36</sub>P<sub>2</sub>Pt requires: C, 60.86; H, 4.84; P, 8.27; Pt, 26.03 %).

vii) *Bis (triphenyl phosphine) chloro (methyl) platinum(II)*: (PPh<sub>3</sub>)<sub>2</sub>PtCl(Me).

An identical reaction as in (vi) between diammonium (methylpentafluorosilicate) and dichlorobis (triphenyl phosphine) platinum(II) in 1:1 molar ratio, gave the title product (70 %) mp. 274° (dec.) (Found: C, 57.53; H, 4.29; Cl, 4.60; P, 8.00; Pt, 25.40; C<sub>37</sub>H<sub>33</sub>ClP<sub>2</sub>Pt requires: C, 57.69; H, 4.32; Cl, 4.59; P, 8.04; Pt, 25.36 %).

viii) *Bis (triphenyl phosphine) diphenylplatinum(II)*: (PPh<sub>3</sub>)<sub>2</sub>PtPh<sub>2</sub>.

In an identical reaction as in (vi) between diammonium (phenylpentafluorosilicate) and dichlorobis (triphenyl phosphine) platinum(II) in 2:1 molar ratio, the desired product was obtained (70 %) mp. 158-60° (dec.) (lit. [12<sup>c</sup>], mp. 160°) (Found: C, 65.90; H, 4.55; P, 6.99; Pt, 22.20; C<sub>48</sub>H<sub>40</sub>P<sub>2</sub>Pt requires: C, 65.97; H, 4.61; P, 7.09; Pt, 22.33 %).

ix) *[1,2-Bis (diphenyl phosphino) ethane] dimethylplatinum(II)*: (PPh<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PtMe<sub>2</sub>.

From a similar reaction as in (vi) between dichloro-[1,2-bis (diphenyl phosphino) ethane] platinum(II) and diammonium (methylpentafluorosilicate) in 1:2 molar ratio, the desired product was isolated (80 %) mp. 220-250 (lit. [12<sup>c</sup>], mp. 221-23°) (Found: C, 53.90; H, 4.60; P, 9.81; Pt, 31.00; C<sub>28</sub>H<sub>30</sub>P<sub>2</sub>Pt requires: C, 53.93; H, 4.85; P, 9.93; Pt, 31.29 %).

x) *[1,2-Bis (diphenyl phosphino) ethane] diphenylplatinum(II)*: (PPh<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PtPh<sub>2</sub>.

In an identical reaction as in (vi) between diammonium (phenylpentafluorosilicate) and dichloro [1,2-bis (diphenyl phosphino) ethane] platinum(II) in 2:1 molar ratio, the desired product was obtained

(75 %) mp. 210-14° (lit. [12<sup>g</sup>], mp. 207-12) (Found: C, 60.90; H, 4.40; P, 8.20; Pt, 25.98; C<sub>38</sub>H<sub>34</sub>P<sub>2</sub>Pt requires: C, 61.02; H, 4.59; P, 8.29; Pt, 26.10 %).

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