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Preliminary communication

PREPARATION OF NEW HYDRIDOPLATINUM(II) CARBENE DERIVATIVES FROM HYDRIDOTRIFLUOROMETHYL COMPLEXES

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Summary

New stable cationic hydridoplatinum(II) carbene complexes of the general formula *trans*-$PtH(carbene)(PPh_3)_2^+$ (carbene = $C(OMe)_2$, $\overline{CO(CH_2)_nO}$, n = 2,3, $\overline{CSCH_2CH_2S}$) have been prepared by reaction of *trans*-$PtH(CF_3)(PPh_3)_2$ with HBF_4 in Et_2O in the presence of an excess of monofunctional or bifunctional alcohols or thioalcohols. Analogous reactions using *trans*-$PtCl(CF_3)(PMe_2Ph)_2$ gave the chloroplatinum(II) carbene complexes *trans*-$PtCl(carbene)(PMe_2Ph)_2^+$ (carbene = $C(OMe)_2$, $\overline{COCH_2CH_2O}$).

There appear to be only a few hydrido-transition metal carbene complexes in the literature [1—3], and these mostly had platinum as the central metal. The carbene ligand was incorporated into these species by interaction of a metal substrate with an electron-rich olefin [1b] or by nucleophilic attack of amines or alcohols on a metal-coordinated isocyanide [2] or acetylene [3] ligand, respectively.

In our search for structure-reactivity correlations for hydrido-organoplatinum derivatives containing electronegatively-substituted alkyl groups of the type $PtH(R_x)L_2$ (R_x = cyanoalkyl; L = tertiary phosphine or 1/2 diphosphine) [4], we examined the ability of fluoroalkyl ligands to stabilize platinum(II) metal complexes containing the hydride ligand. We found that the complex *trans*-$PtH(CF_3)(PPh_3)_2$ [5] shows increased sp^3 C—F bond lengths [6] and reduced C—F stretching frequencies in the IR [5]. This phenomenon has been studied in detail [7,8] for other perfluoroalkyl-transition metal complexes, and has been invoked to explain the ability of the C—F bonds α to the transition metal to undergo electrophilic attack to produce highly reactive difluorocarbene derivatives [9—11] or to participate in halogen exchange with Lewis acids [12].

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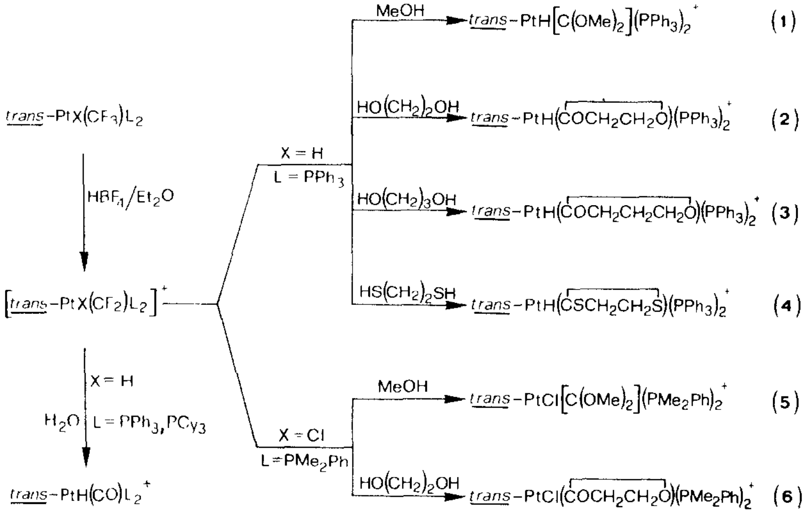
Electrophilic attack on *trans*-PtH(CF$_3$)(PPh$_3$)$_2$ by protic electrophiles of the type HX (X = Cl, BF$_4$) can involve different processes depending on the nature of the anion X. When X = Cl selective cleavage of the Pt—CF$_3$ bond occurs [5]. When X = BF$_4$ the reaction involves the C—F bonds, and produces a highly reactive difluorocarbene intermediate, which is subsequently attacked by protic nucleophiles such as methanol, diols, dithiols or water to give dioxo-, dithiocarbene and carbonyl complexes, respectively. The preliminary results of this study are reported below.

A fast reaction takes place upon treatment of *trans*-PtH(CF$_3$)(PPh$_3$)$_2$ at room temperature with an ethereal solution of HBF$_4$ in dry Et$_2$O in the presence of excess methanol, diols, dithiols or water, to give high yields of stable cationic hydridoplatinum(II) carbene or carbonyl complexes, as shown in Scheme 1.

SCHEME 1



The proposed intermediate, a difluorocarbene complex *trans*-PtH(CF$_2$)-(PPh$_3$)$_2$$^+$ would undergo nucleophilic attack by the various protic O- or S-donors to give the final stable products. Such a two-step reaction pathway has been clearly demonstrated for trifluoromethylruthenium complexes [10], for which the relatively stable difluorocarbene intermediate could be isolated. In our systems many attempts to provide direct evidence for such a difluorocarbene ligand were unsuccessful, probably owing to the enhanced electrophilicity of the difluorocarbene carbon in the cationic intermediate complex.

The *trans* configuration of the carbene derivatives *trans*-PtH(carbene)(PPh$_3$)$_2$$^+$ is readily deduced from ^{1}H and ^{31}P NMR data (Table 1). In addition, these complexes show ν(Pt—H) stretching frequencies in CH$_2$Cl$_2$ in the 2076—2088 cm^{-1} range. These data, coupled with ^1J(Pt—H) values, confirm that the *trans* influence of the carbene ligands [1a,3,13] is higher than that of neutral ligands (L′) such as CO, CNR or phosphines in cationic complexes of the type *trans*-PtH(L′)-(PR$_3$)$_2$$^+$ [14].

TABLE 1

^{1}H, ^{31}P NMR AND IR SELECTED DATA FOR THE NEW PLATINUM(II) CARBENE COMPLEXES

Complex [a]	^{1}H NMR [b]				^{31}P{^{1}H}NMR [b]		IR (cm^{-1})	
	δ(H)	^1J(H—Pt)	^2J(H—P)	δ(other)	δ(P)	^1J(P—Pt)	ν(Pt—H) [c]	ν(Pt—Cl) [d]
1	−6.90(t)	650	12.9	4.00(br) [e],3.24(br) [e]	24.3(s)	2787	2082(m)	
2	−6.40(t)	686	12.9	3.90(s) [f]	25.8(s)	2784	2088(m)	
3	−7.68(t)	659	13.9	3.69(t) [g],1.37(q) [h]	26.5(s)	2845	2076(m)	
4	−6.22(t)	699	11.8	3.06(s) [i]	28.4(s)	2800	2079(m)	
5				3.91(br) [j],1.97(t) [k]	−7.8(s)	2243		313(m)
6 [l]				4.03(s) [m],1.94(t) [n]	−5.3(s)	2229		326(m)

[a] Satisfactory elemental analyses have been obtained for all the complexes prepared. [b] Spectra recorded in $CDCl_3$ (+25°C) unless otherwise stated and referenced to Me_4Si (^{1}H) and 85% H_3PO_4 (^{31}P); δ in ppm, J in Hz; negative chemical shifts are upfield from the reference used; s, singlet; t, triplet, br, broad; q, quintet. [c] In CH_2Cl_2, m, medium. [d] Nujol mull, m, medium. [e] δ(OCH_3). The two signals, owing to the unequivalence of the OCH_3 groups, show up as sharp singlets at −40°C (δ 4.01 and 3.21), while only one singlet is observed in CD_3CN at +80°C (δ 3.73). [f] δ(OCH_2), ^4J(H—Pt) 4.5. [g] δ(OCH_2), ^3J(H—H) 5.5. [h] δ(CH_2), ^3J(H—H) 5.5. [i] δ(SCH_2), ^4J(H—Pt) 6.3. [j] δ(OCH_3). The signal appears as a sharp singlet at +74°C in CD_3CN (δ 4.00, ^4J(H—Pt) 7.4.). [k] δ(P—CH_3), ^2J(H—P) + ^4J(H—P) = 8.1, ^3J(H—Pt) 28.5. [l] NMR in CD_2Cl_2. [m] δ(OCH_2), ^4J(H—Pt) 8.6. [n] δ(P—CH_3), ^2J(H—P) + ^4J(H—P) = 8.3, ^3J(H—Pt) 27.3.

Similar reactions carried out on complexes of the type *trans*-$PtH(CF_3)L_2$ (L = PPh_3, PCy_3) in wet ethereal suspensions gave quantitative yields of the cationic hydridocarbonyl derivatives *trans*-$PtH(CO)L_2^+$ (L = PPh_3 [15]; L = PCy_3 [3]).

In order to gain more information on the role of electronic and/or steric factors in affecting this type of reactivity of the CF_3 group in platinum complexes, we examined also the reactions of complexes of the type *trans*-$PtCl(CF_3)L_2$ (L = PPh_3 [16], $PMePh_2$ [16], PMe_2Ph [17]). Preliminary results indicate that only the derivatives containing the more basic phosphorus PMe_2Ph react, under the conditions used for *trans*-$PtH(CF_3)(PPh_3)_2$, to give the corresponding chloroplatinum(II) carbene species *trans*-PtCl(carbene)$(PMe_2Ph)_2^+$ (carbene = $C(OMe)_2$ (5); $\overline{COCH_2CH_2O}$ (6)), albeit in low yield.

The method described above provides an easy direct route to a variety of carbene complexes of platinum(II). Further work on the synthesis of other metal-carbene complexes and their reactions with nucleophiles is underway.

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